AD NUMBER
AD475842
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to DoD and DoD contractors only; Administrative/Operational Use; JUL 1965. Other requests shall be referred to Air Force Materials Lab., Wright-Patterson AFB, OH 45433.
AUTHORITY
AFML ltr, 7 Dec 1972

475842

HIGH TEMPERATURE RESISTANT ELASTOMER COMPOUNDS

Marlyn J. Brock
David L. Jividen
Floyd M. Smith
Jack D. Rigby
George R. Thurman

The Firestone Tire & Rubber Company

TECHNICAL REPORT AFML-TR-65-178

JULY 1965

NOTICES

HIGH TEMPERATURE RESISTANT ELASTOMER COMPOUNDS

Marlyn J. Brock
David L. Jividen
Floyd M. Smith
Jack D. Rigby
George R. Thurman

The Firestone Tire & Rubber Company

FOREWORD

This report was prepared by the Central Research Laboratories of The Firestone Tire & Rubber Company, Akron, Ohio, under USAF Contract No. AF 33(657)-10419. The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734005, "Elastomeric and Compliant Materials." The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with W. F. Anspach as the Project Engineer.

This report covers work conducted from 1 January 1964 to 31 December 1964.

Manuscript released by the authors April 1965 for publication as an AFML Technical Report.

This technical report has been reviewed and is approved.

J. M. KELBLE, Chief
Elastomers and Coatings Branch
Nonmetallic Materials Division
AF Materials Laboratory

ii

ABSTRACT

The mechanism by which butyl rubber undergoes thermal degradation in the temperature region 300° to 400°F has been investigated. Gas chromatograph techniques have been used to identify the degradation products and to determine their rates of formation. This investigation indicates that degradation upon heating may be initiated at (a) reactive sites already present in the polymer such as catalyst residues, branching, and terminal unsaturation, (b) oxygenated groups such as hydroperoxides formed during exposure to oxygen and which are unstable at low temperature and (c) other oxygenated groups more stable than hydroperoxides and which do not decompose below 400°F. Compounding evaluations were made of resin cured butyl, reclaimed silicone rubber and ethylene-propylene rubber. A high temperature, high vacuum stress relaxation apparatus was designed and constructed. A limited evaluation program has indicated that the design is satisfactory and the apparatus should prove useful for evaluation of polymers in high vacuum (10^{-5} Torr) and at temperatures up to 500°F. Minor modification would permit testing in an inert gas atmosphere.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The object of this work is to continue the evaluation of high temperature resistant elastomers and elastomer compounds suitable for a variety of applications which arise in missiles and high speed aircraft. The investigation of the decomposition mechanisms in the temperature range 300° to 400°F, where loss in physical properties is first noted, should lead to a better understanding of the requirements for high temperature resistant elastomers.

Stress relaxation measurements have often been used to investigate the effects of time and temperature on the physical properties of elastomers. In order to attain a better understanding of the effect of oxygen at elevated temperatures a stress relaxation apparatus was designed and built which would permit tests to be conducted at vacuum as low as 10^{-5} Torr and temperatures as high as 500°F.

SECTION I

LOW TEMPERATURE DEGRADATION INVESTIGATIONS
OF POLYISOBUTENE AND POLYISOBUTENE VULCANIZATES

The object of the current research program is to determine the mechanism by which butyl rubber undergoes thermal degradation in the temperature region 150^C to $200^{\circ}C$ (300° to $400^{\circ}F$) where the loss of physical properties is first noted and to learn more about the role oxygen plays during polymer degradation. Butyl vulcanizates and polyisobutene with various oxidative histories were subjected to thermal degradation in this temperature region. Identification of the degradation products and their rates of formation were determined chromatographically. It is hoped that elucidation of the mechanism by which these materials degrade will be of value to the improvement of the thermal stability of butyl elastomers and ultimately other polymer systems.

Madorsky and coworkers reported the results of their pyrolysis studies of polyisobutene, polyisoprene, polybutadiene, SBR and polyethylene in 1949 (1). This work was carried out in a high vacuum at 300° to $500^{\circ}C$. Although the presence of both CO and CO_2 were reported in the pyrolysis products of the purified polymer, no significance is attached to their presence in subsequent decomposition mechanisms which were proposed. As a result of these and other studies, a polymer degradation theory gradually evolved.

In general, polymer degradation may be considered as a reverse polymerization consisting of 1) initiation, 2) propagation, 3) transfer, and 4) termination reactions as proposed by Simha, Wall and Blatz (2) and others (3). The reactions are summarized below.

1) Initiation -- Radicals Formed by Rupture

    $P-CH_2-CHX-CH_2-CHX-P \longrightarrow P-CH_2-CHX \cdot$ and $P-CHX-CH_2 \cdot$
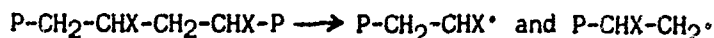
2) Propagation -- Monomer Fragments Split Off Stepwise Along the Chain

    $P-CH_2-CHX-CH_2-CHX \cdot \longrightarrow P-CH_2-CHX \cdot + CH_2 = CHX$
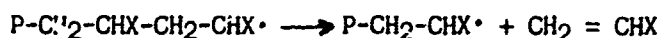
3) Transfer -- Competitive With Propagation Reaction

    A. Intermolecular

    $P-CHX \cdot + P-CH_2-CHX-CH_2-CHX-P \longrightarrow P-CH_2X + P-CH_2-CX = CH_2 + \cdot CHX-P$

    B. Intramolecular

    $P-CHX-CH_2-CHX-CH_2-CHX \cdot \longrightarrow P-CHX \cdot + CH_2 = CX-CH_2-CH_2X$

2
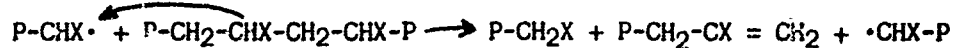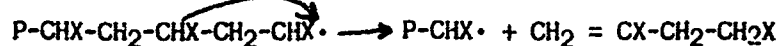
4) Termination

    A. Recombination

$$P-CH_2-CHX\cdot + P-CHX-CH_2\cdot \longrightarrow P-CH_2-CHX-CH_2-CHX-P$$
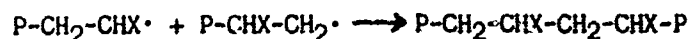
    B. Radical Disproportionation

        2 Radicals $\longrightarrow$ 2 Polymers

Simha, Wall and Blatz (2) have developed rate equations which follow the reactions shown above.

Jellinek (3) has also developed a theory of depolymerization assuming a chain process which is similar but also differs in many respects from that of Simha and coworkers. One of the principal differences is that initiation in the Simha theory is represented as a main chain carbon-carbon bond scission. Jellinek proposes a mechanism for the degradation of polystyrene which is dependent upon the presence of weak links along the polystyrene chain which results from the incorporation of oxygenated groups.

Tolbclsky and coworkers (4), as early as 1942, showed that there is a relationship for most polymers, including butyl rubber, between moles of oxygen absorbed and the moles of chain cleavage produced. Data presented in this work shows that under maximum rate conditions of oxidation and chain scission, the ratio of moles of oxygen absorbed to moles of chain scission is near unity for a butyl vulcanizate except in ie very early stages of oxidation where measurements are admittedly less precise. These results are evidence that the previous oxidative history of a polymer could play an important role in subsequent degradation studies.

Wall and Florin (5) state in summarizing their degradation work that "On qualitative grounds it is evident that the pyrolytic behavior of polymers studied is a result of their basic structure and not of trace impurities or structures, at least within certain limits." This statement may be true for high temperature degradations, but it is open to question for low temperature degradations involving small amounts of decomposition requiring lower activation energies. Much evidence indicates that such initiation takes place at weak links produced by small irregularities in the polymer structure such as branching (6) or the presence of oxygenated groups (7).

Additional references related to the thermal degradation of polymers are listed in the Bibliography section.

To date, most polymer degradation studies have been carried out in a vacuum at temperature ranges from 300° to 500°C with decomposition rates varying from 0.1% to 1 or 2% per minute. However, it is well known that rubber vulcanizates lose physical properties at much lower temperatures (150° to 200°C) and long before 1% of the material has been volatilized away. The work described in this report is primarily concerned with this lower temperature region.

3

TEST METHODS AND APPARATUS

Samples of butyl vulcanizate and poly isobutene were aged in air at elevated temperatures then subjected to progressive isothermal aging (PIA) from 100° to 250°C in an inert atmosphere*. PIA was first carried out in a pyrolysis tube heated by a Fisher furnace (8), however, condensation of the higher molecular weight volatiles in the cooler parts of this system prevented an accurate determination of their relative rates of evolution during PIA. A new furnace was, therefore, designed and built to maintain the entire system at the aging temperature. The furnace was constructed from a 4 by 6 by 8 inch aluminum block (Figure 1). Four cavities were drilled into one side of the block to house four 250 watt cartridge heaters. Two cavities were drilled in the front of the block to serve as a sample chamber and to house a thermocouple. The sample chamber is fitted with an injection port machined from a piece of hexagonal brass stock. A silicone rubber septum is used to seal the injection port and to permit the injection of gases into the sample cavity. A large cavity was also machined in the top of the furnace to house a two way teflon sleeve valve and associated plumbing. The valve is connected to the sample chamber and to a second valve mounted outside the furnace. By manipulation of these valves the chromatographic carrier gas can be directed through the sample chamber or through a bypass loop directly to the chromatograph. The temperature of the furnace is controlled by an F & M Power Proportioning Temperature Programmer.

The chromatographic system (Figure 2) consists of an F & M High Temperature Chromatograph in series with an ambient temperature chromatograph (ATC). The F & M chromatograph is fitted with a 7 foot SE-30 column and the ATC is equipped with a 15 foot DMS and a 10 foot silicone grease column connected in series. A carrier gas flow rate of 65 ml./min. was used. The F & M column is normally maintained at 250°C. At this temperature air, CO_2, and low molecular weight hydrocarbons are recorded as a single peak. Higher molecular weight volatiles, if present, are recorded as a second peak. The high molecular weight fraction can be separated into its several components by programming the F & M column temperature from ambient temperature to 250°C. The components of the low molecular weight fraction are separated by the ATC. A dry ice trap has been placed between the chromatographs to prevent the high molecular weight volatiles from entering the ATC. A molecular sieve column incorporated into the ATC system provides separation of O_2, N_2, methane and CO which are otherwise recorded as a single "air" peak using the DMS-silicone grease column. An 18 inch DMS loop is used as a bypass for the molecular sieve column. The carrier gas stream through the column is controlled by a two way valve. When it is desired to separate the components of the "air" peak, the gas stream is first directed through the molecular sieve column, then when it has been determined that all of the volatiles under the "air" peak have entered the molecular sieve column, the gas stream carrying CO_2 and low molecular weight hydrocarbons is bypassed to the ATC. Oxygen, N_2, methane and CO are stored in the molecular sieve column while the other volatiles are being analyzed by the ATC. After the last hydrocarbon peak, i.e. isobutene, is recorded the carrier gas is

---

* Under the PIA sequence the aging temperature is increased in 25°C increments every 30 minutes. The volatiles produced during PIA are identified chromatographically.

4
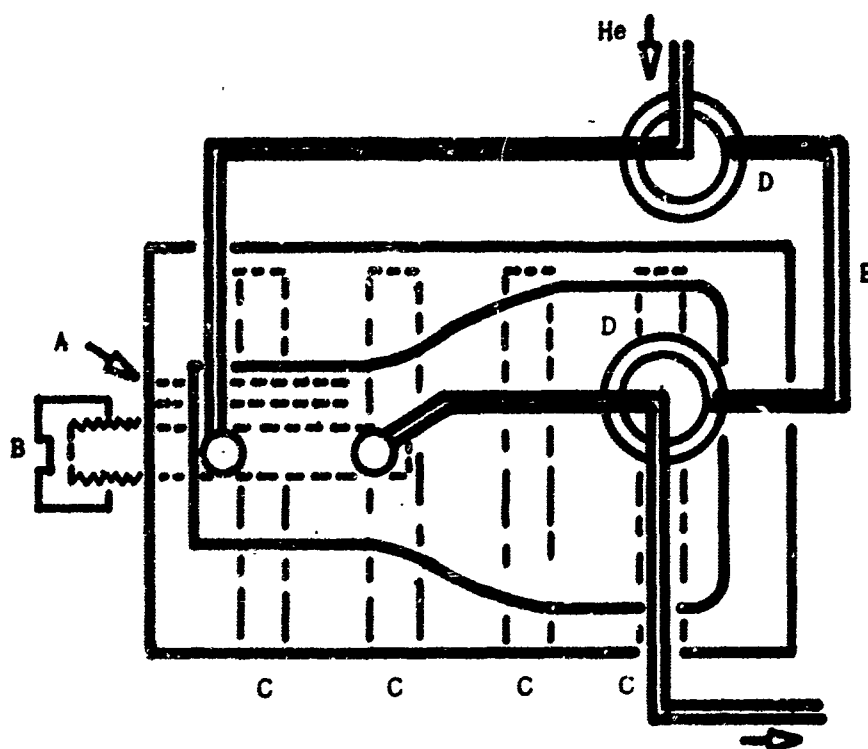
A Aluminum block 4 x 6 x 8 inches

B Injection port and opening to sample chamber

C 250 Watt cartridge heaters

D 2 way valves

E Furnace bypass

Figure 1. Aluminum Block Aging Furnace
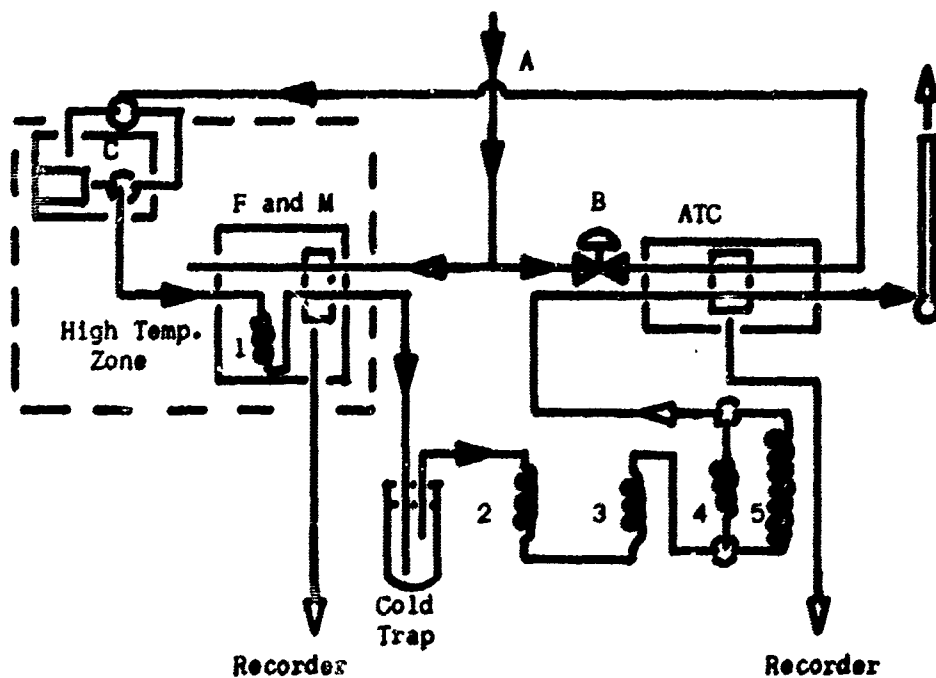
A Helium supply

B Flow regulator

C Aging furnace (figure 1)

1 7' SE 30 silicone column

2 10' Silicone grease column

3 15' DMS column

4 3' DMS bypass column

5 10' Molecular sieve column

Figure 2. System for Analysis of Total Volatiles

re-routed through the molecular sieve column and the stored volatiles are swept into the ATC for detection and recording on the chromatogram.

The volatile degradation products formed during PIA are sampled by sweeping the sample chamber of the aging furnace with the chromatographic carrier gas for 30 seconds. Samples are normally taken every 15 minutes during the PIA sequence. Between samples the volatile degradation products are stored in the sample chamber. In this way the volatiles are concentrated and degradation as evidenced by evolution of hydrocarbons can be detected at much lower temperatures than was previously possible.

Total pyrolysis of polyisobutene and butyl vulcanizate was carried out at 1000°C using the F and M Model 80 pyrolysis unit. A sample was placed in the resistance probe of the pyrolysis unit which was then inserted into the injection port of the F and M chromatograph. The temperature of pyrolysis was controlled by the amount of current passed through the probe during ignition. The degradation products were identified by the above chromatographic system except that the F and M chromatograph was fitted with a 10 foot silicone grease column and the ATC with a 15 foot DMS column.

The rates of evolution of volatiles were determined directly from the chromatograms. The rate of evolution curves for the various volatiles produced during PIA were obtained by plotting the chromatographic peak height, in millimeters per each 15 minute accumulation period, versus temperature on semilog paper.

The percent ditertiarybutylparacresol (DBPC) was obtained by extracting polymer samples for 16 hours with absolute ethanol. The extract was then diluted with additional ethanol and the percent DBPC was determined by absorbtion in the ultraviolet region using a Beckman DK-2 spectrophotometer.

DISCUSSION OF RESULTS

Pyrolysis of Polyisobutene and Butyl Vulcanizates

The more volatile degradation products from the total pyrolysis of butyl vulcanizates at 1000°C have been identified by gas chromatographic techniques as methane, CO, ethane and/or ethene, CO_2, propane, propene, isobutene, n-butane, neopentane and isobutene. These products with the exception of the C_2 and C_3 hydrocarbons agree with the volatile products obtained by Madorsky and coworkers [1]. Isobutene is the major volatile pyrolysis product obtained under these conditions. Polyisobutene and butyl vulcanizates produced the same relative amounts of volatile products.

Production of Higher Molecular Weight Degradation Products

Madorsky et al [1] also obtained fractions of higher molecular weight material in their pyrolysis studies. One fraction was assumed to be dimer and trimer while another contained material having an average molecular weight of 543 which most likely contained polymer fragments consisting of 9 - 10 monomer units.

7

Higher molecular weight fragments were also observed in the current studies such as dimer, trimer and material having a molecular weight as high as 320. Most raw polymers produced a small amount of higher molecular weight products which in part consisted of the antioxidant. Fully compounded vulcanizates produced a larger quantity of higher molecular weight products which in part could have been derived from the compounding ingredients. No attempt was made to make a thorough study of the higher molecular weight volatile products produced on aging.

For the most part low temperature studies produced only small amounts of the higher molecular weight degradation products. The results reported here have been obtained from a study of the evolution rates of the more volatile products produced, mainly CO_2 and isobutene.

Low Temperature Degradation Studies

It has been shown that most polymer vulcanizates exhibit a loss in physical properties when they are aged in air at elevated temperatures. An attempt was made to correlate the temperature range where this loss in physical properties is observed with the volatile products which are produced during PIA. Samples of butyl vulcanizate were aged in an air oven for eight hours at temperatures ranging from 275° to 400°F. The physical properties of the aged samples are shown in Table 1. In Figure 3 the tensile strengths of these samples are plotted versus aging temperature. Also plotted in Figure 3 are the CO_2 and isobutene evolution rates for the unaged and aged samples as determined by PIA. These data show that degradation as measured by physical properties occurs at temperatures above 325°F. Figure 3 also indicates that the rate of evolution of volatiles increases at aging temperatures above 325°F. An increase in the evolution rate of CO_2 is observed for the unaged sample as low as 300°F. Isobutene is first observed at 390°F with the unaged sample. Greater sensitivity could have been obtained in the above experiments provided the volatile samples had been accumulated for periods longer than 15 minutes before chromatographic analysis.

These results show that the decrease in physical properties of a butyl vulcanizate at elevated temperatures can actually be correlated with the evolution of volatile decomposition products. Figure 3 also indicates that aging in air increases the rate of evolution of isobutene which is observed during PIA aging.

The Effect of Exposure to Oxygen on the Degradation of Polyisobutene

Samples of polyisobutene (Vistanex L 80) were aged in an air oven at 400°F for 2, 4 and 8 hours. These samples were then subjected to PIA aging. The rate of evolution of CO_2 and isobutene which occurred during PIA aging is shown in Figure 4. The evolution of isobutene before exposure to air at elevated temperatures is not detected much below 200°C during PIA. However, after air aging, the evolution of isobutene can be detected as low as 100°C. Furthermore the rate of evolution of volatiles is a function of the degree to which the sample has been aged as shown in Figure 4. Figure 4 indicates that the evolution of CO_2 with temperature increases up to about 200°C then levels off. The rate of evolution of isobutene increases up to 150°C, levels off to about 175°C and then increases again as the temperature is raised from 200° to 250°C.

8

TABLE 1

PHYSICAL TESTING DATA OBTAINED FROM BUTYL VULCANIZATES
BEFORE AND AFTER AGING 8 HOURS IN AIR AT VARIOUS TEMPERATURES

Compound Formula: 100 Enjay Butyl 268, 50 HAF black, 3 zinc stearate, 3 Polar Oil 45, 5 zinc oxide, 12 Amberol ST-137, 1.3 $SnCl_2 \cdot 2H_2O$ (75%).

Cured: 60 min. @ 320°F

Test Temperature: 73°F

Aging Temperature, °F	Tensile Strength psi	300% Modulus psi	Ultimate Elongation %
---	2250	1350	420
???	2150	1800	375
300	3075	2550	350
325	2175	2000	340
350	1925	----	290
375	1725	----	280
400	1125	----	245

9

Tensile Strength vs Temperature

□ Tensile Strength vs Temperature
◇ CO_2 Peak, Unaged Stock
○ CO_2 Peak, Aged Stock
◖ Isobutene Peak, Unaged Stock
△ Isobutene Peak, Aged Stock

Peak Height
mm/10' Accumulation

70
60
50
40
30
20
10
0

Tensile
#/in²

3100
2800
2500
2200
1900
1600
1300
1000

140   150   160   170   180   190   200   210   220
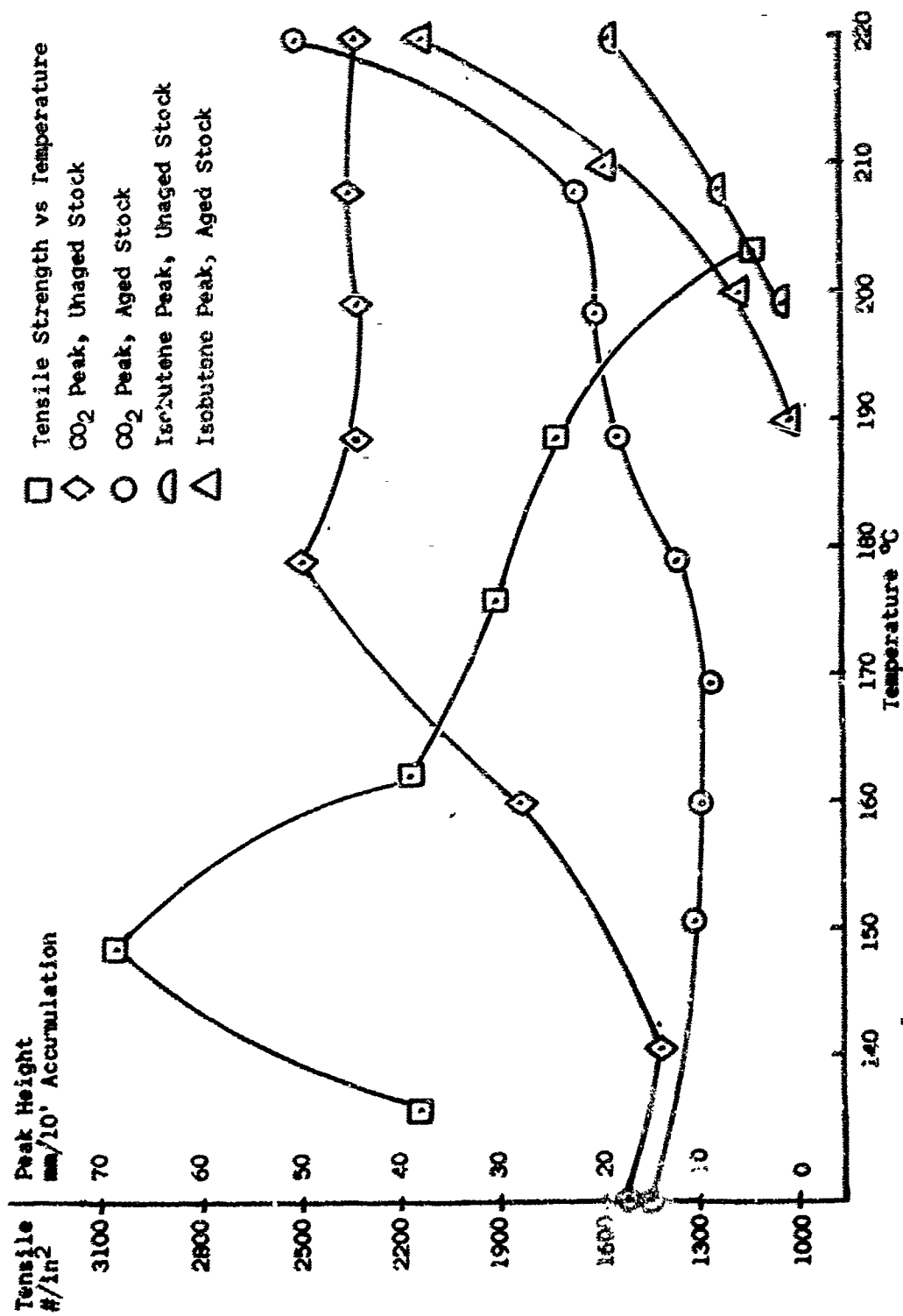
Temperature °C

Figure 3. Evolution of CO_2 and Isobutene from Butyl Vulcanizate vs Loss of Tensile Strength

10
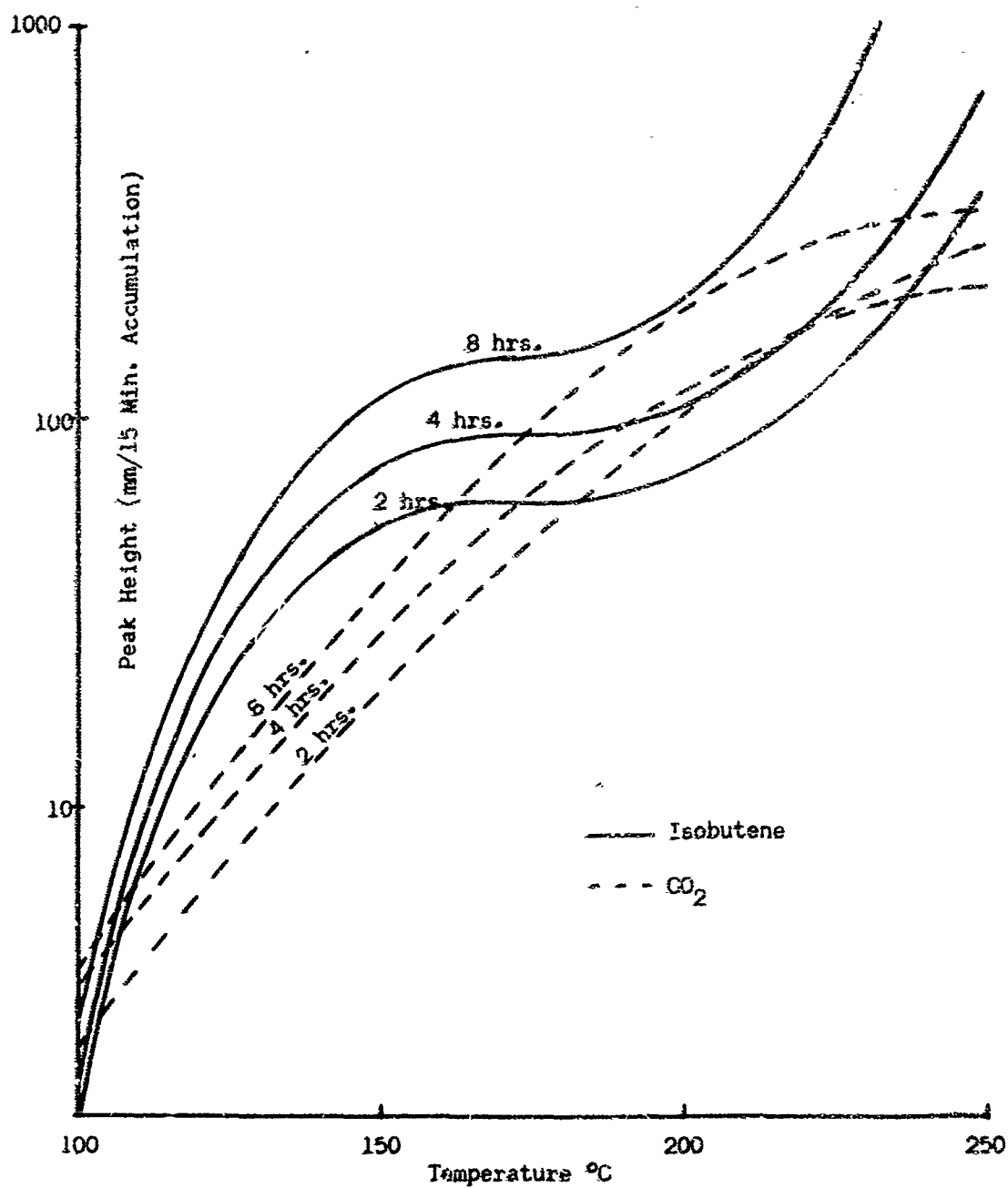
Figure 4. The Effect of Aging on the Evolution of Volatiles from Vistanex L-80

Samples Aged in Air at 400°F for 2, 4 and 8 Hours

11

These results indicate that there may be two different degradation mechanisms involving two different types of oxygenated sites of different stabilities which initiate the decomposition of oxidized polyisobutene.

A series of PIA cycles, shown graphically in Figures 5 and 6, was carried out to investigate this behavior further. In this series of experiments a sample of the polymer was aged in air for 8 hours at 200°C, then subjected to several PIA cycles without additional exposure to oxygen. From Figure 5 it can be seen that during each successive PIA cycle the rate of evolution of isobutene decreases rapidly at the lower temperatures until the characteristic rate of evolution curve shown in Figure 4 has disappeared and the rate of evolution curve approaches that obtained for the unaged sample.

Exposure of the same sample to air for a second time produced similar results (Figure 6). This indicated that during the first aging period a number of sites are oxidized, however, a great number of reactive sites must still remain. These sites may then be attacked during the second air aging period. During PIA the less stable oxygenated sites decompose to initiate a relatively rapid rate of degradation of the polymer chains between 100° and 150°C, then as the number of these sites decreases the rate levels off and starts to drop. The more stable oxygenated sites, however, begin to decompose at higher temperatures and result in the increase in rate of evolution of isobutene above 175°C. During subsequent PIA cycles the less stable sites have essentially disappeared and any additional degradation is initiated by the more stable sites still present.

On the basis of these rate of evolution curves (Figure 4), it seems reasonable that if the air aged polymer were heated at 175°C, in an inert atmosphere it could in effect be "deactivated", i.e. the less stable oxygenated sites responsible for initiating degradation below 175°C could be decomposed leaving only the more stable oxygenated sites. These stable sites should then decompose and initiate thermal degradation of polyisobutene at temperatures above 175°C. This was found to be the case as shown in Figure 7. Heating polyisobutene for 16 hours at 175°C in a dynamic helium atmosphere reduced the rate of evolution of CO_2 and isobutene to very low levels. However, upon raising the temperature to 250°C the rate of evolution of isobutene increased rapidly until at 250°C the evolution rate was nearly equal to the sample of polyisobutene which had not been deactivated.

Degradation of Raw Polymer Versus Vulcanizate

Figure 7 shows the PIA curves for butyl vulcanizate R142325 and black masterbatch L 80.

Both samples exhibit a much lower rate of isobutene evolution during PIA than the raw Vistanex L 80 polymer. The early rise in the rate of evolution curve, as seen in the case of the raw polymer, is absent. These results indicate that compounding and curing or even the presence of carbon black has a stabilizing influence upon the raw polymer. Carbon black itself appears to act as an antioxidant and even prevents the early rise in the rate of evolution curve exhibited by the raw polymer Vistanex L 80. Apparently carbon black prevents the formation of the oxygenated sites which are unstable below 175°C in addition to reducing the concentration of oxygenated sites which decompose at higher temperatures.

12

Figure 5. The Effect of Oxidation on the Evolution of Isobutene

First Exposure to Air at 400°F

13

Figure 5. The Effect of Oxidation on the Evolution of Isobutene

Second Exposure to Air at 400°F

14
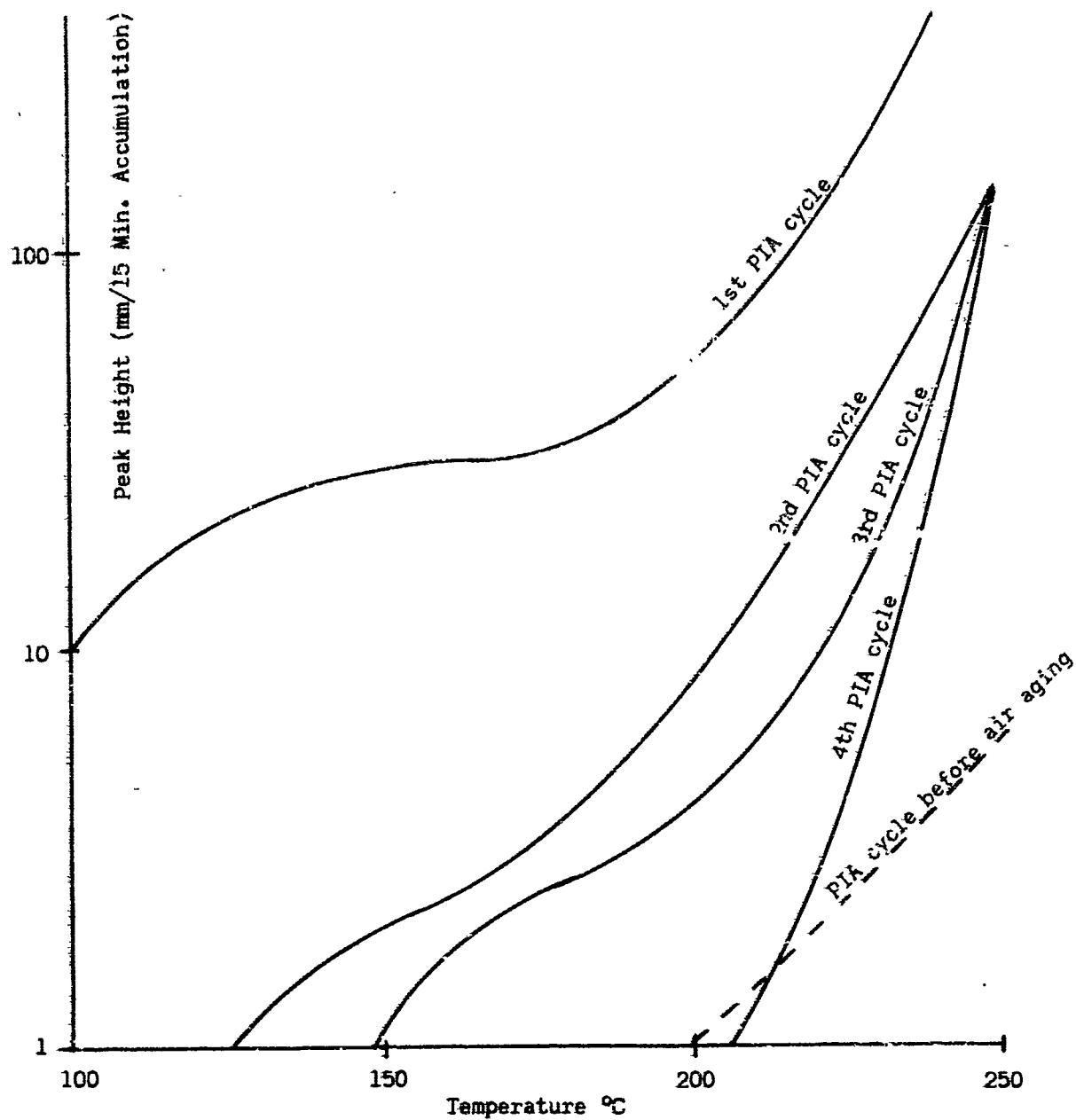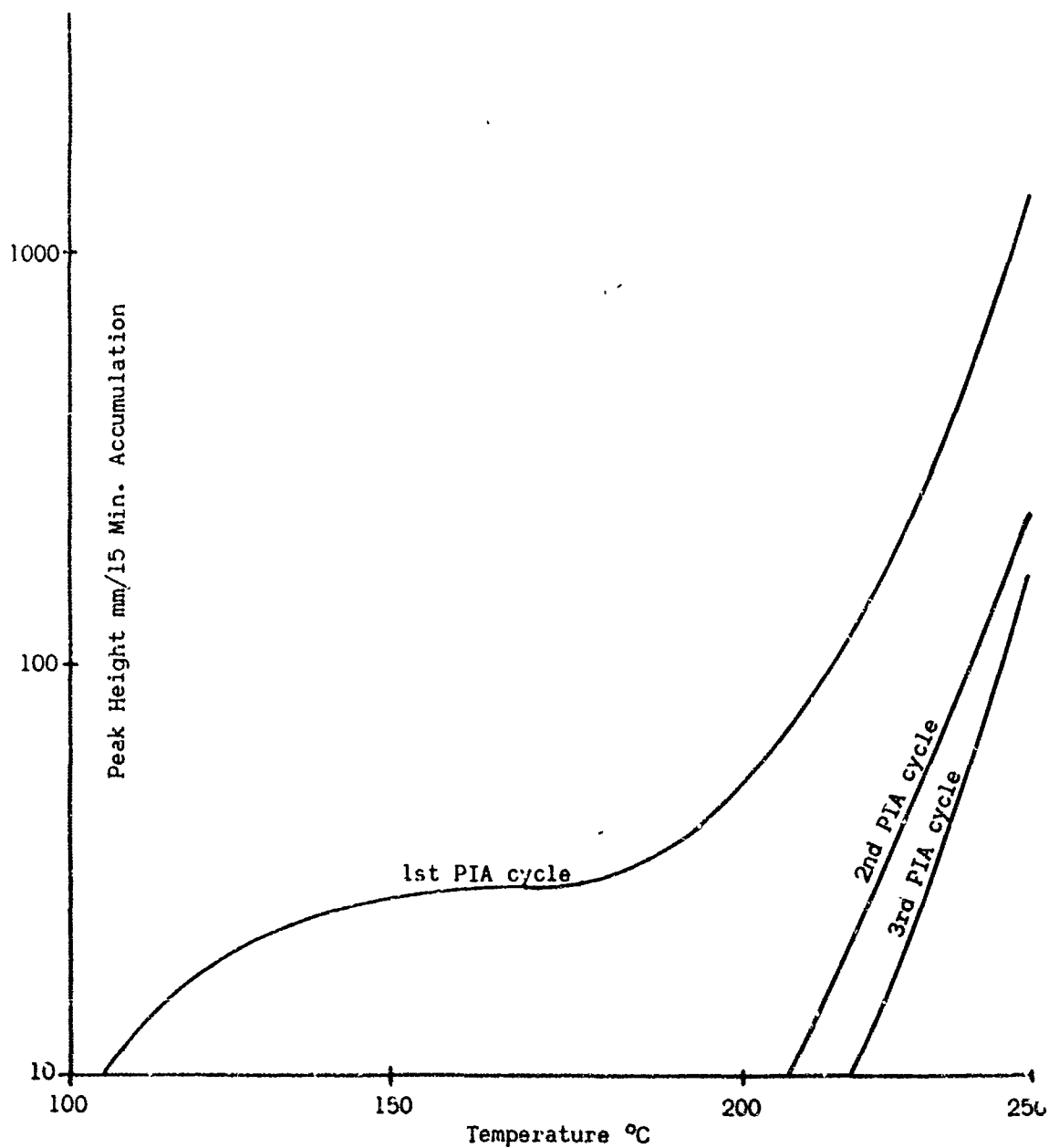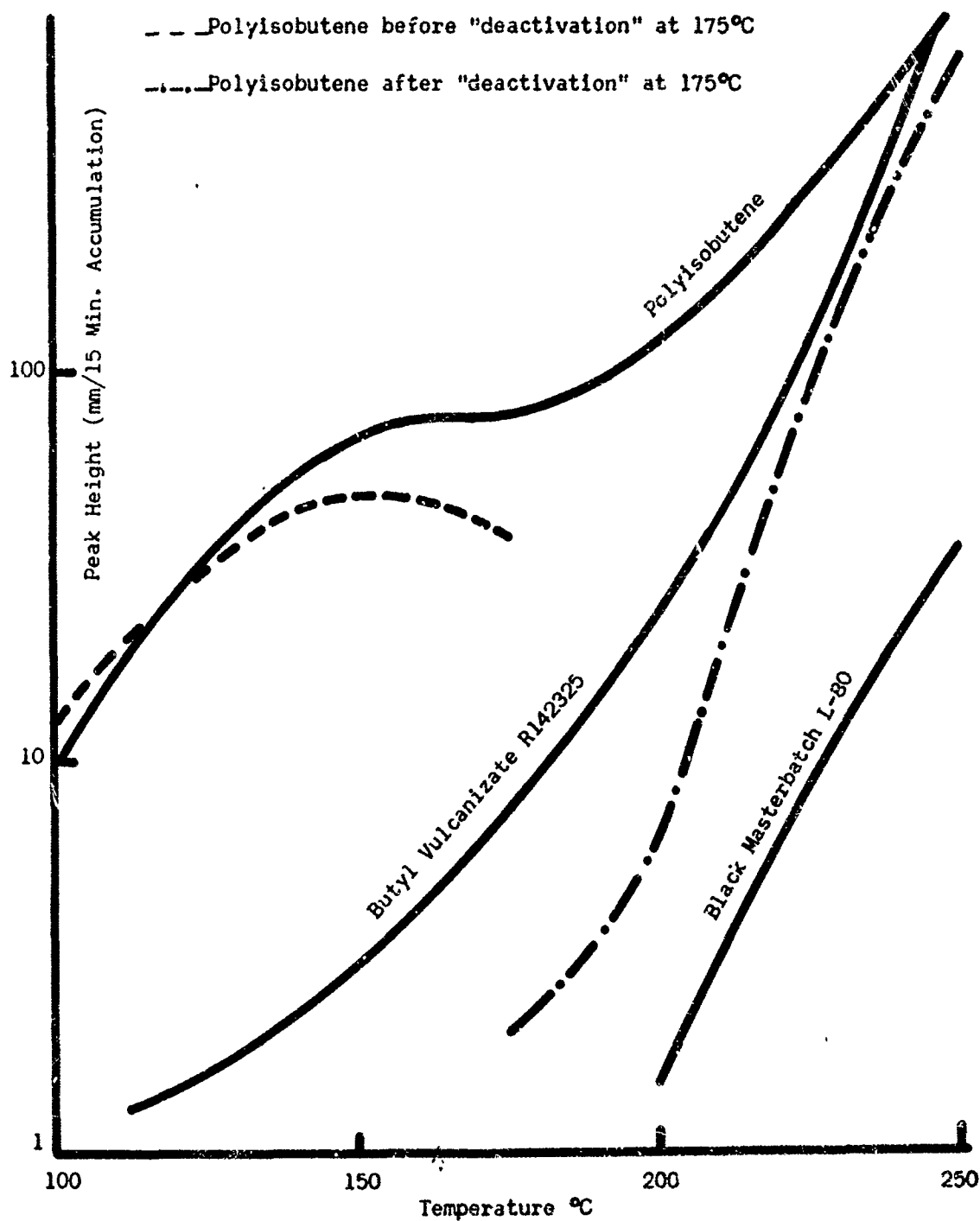
Figure 7. The Effect of Oxidation on the Evolution of Isobutene During PIA
Samples Exposed to Air at 400°F for 8 Hours

15

The Influence of Antioxidants on Oxygen Initiated Degradation

Polyisobutene heated 4 hours at 200°C in the absence of oxygen shows little tendency to degrade. No volatile products are detected during the PIA cycle and the Inherent viscosity (1.92) of the polymer is unchanged before and after aging. However, polyisobutene heated 4 hours at 250°C in an inert atmosphere after a PIA cycle does degrade. A small amount of isobutene is detected during PIA above 200°C and after 4 hours at 250°C the inherent viscosity of the polymer was found to have dropped to 1.64. These results indicate that polyisobutene is stable during aging in an inert atmosphere up to 200°C. However, polyisobutene apparently already contains reactive sites which decompose above 200°C producing chain scission, the evolution of isobutene and a reduction in the inherent viscosity. Such decomposition is not inhibited by the presence of antioxidant, as shown in Table 2. Samples containing 0.8% ditertiarybutylparacresol (DBPC) aged up to 120 hours in air at 100°C show the same initial drop in viscosity but further degradation is prevented by the presence of DBPC. Samples containing less than 0.8% DBPC show additional degradation after only 48 hours aging in air at 100°C (see Table 3). The same indication is given by the rate of evolution of isobutene with samples containing different DBPC concentrations (Figure 8).

The susceptibility of the polymer to oxidation was investigated further by aging samples of polyisobutene protected by antioxidant in air at elevated temperatures. Polymer samples with 0 - 2.3% DBPC were exposed to air for 8 hours at 200°C. However, it was found that under these conditions the antioxidant was quickly depleted and provided little protection. This is evidenced by the fact that the rate of evolution of volatiles from these samples during PIA was very nearly the same regardless of the antioxidant loading. For samples aged in air at 100°C, however, distinct differences were noted. Before air aging the samples were pressed into thin films in order to expose a rather large surface to oxidative attack and to reduce any surface effects due to the low air permeability of polyisobutene. The samples, with 0 - 2.3% DBPC, were then aged in air for 24 - 120 hours at 100°C and subjected to PIA. In order to evaluate more completely the effects of oxidation, PIA cycles were also obtained for unaged samples. It was found that during PIA the unaged samples produced no detectible amounts of isobutene at temperatures below 225°C, however, a higher molecular weight volatile, later determined to be antioxidant, was detected among the volatile products using the F and M chromatograph. Figure 9 shows the rate of evolution of antioxidant from samples containing 0.8, 1.3 and 2.3% DBPC respectively. Figure 9 indicates that antioxidant evolution during PIA begins as low as 100°C and increases rapidly as the aging temperature is increased to 250°C. At 250°C the antioxidant content of the sample would be depleted readily. The percent antioxidant was determined spectrophotometrically before and after exposing a sample of the polymer containing 0.8% DBPC to air at 100°C for 48 hours. It was found that the DBPC content had decreased to 0.033% after 48 hours aging. The fact that isobutene was not detected below 200°C during PIA indicates that sufficient DBPC is still present to prevent degradation.

Curves for the plot of the rate of evolution of isobutene versus temperature are shown in Figure 8. These samples contained different amounts of DBPC antioxidant. Below the 0.8% DBPC level, the samples are not sufficiently protected and a high evolution rate of isobutene is observed at 175°C. The inherent vis-

TABLE 2

INHERENT VISCOSITIES OF POLYISOBUTENE (VISTANEX L80) SAMPLES PROTECTED BY 0.8% DBPC AGED IN AIR AT 100°C

Aging Time (Hrs.)	% DBPC After Aging	Inherent Viscosity (dl/g) After PIA
0	0.30	1.64
24	-	1.93*
24	0.055	1.59
48	0.033	1.56
72	0.027	1.58
96	0.009	1.65
120	none detected	1.69

* Inherent viscosity before PIA. All other samples determined after

  PIA to 250°C and 4 hours in Helium at 250°C.

TABLE 3

INHERENT VISCOSITIES OF POLYISOBUTENE (VISTANEX L80)
WITH 0 - 2.3% DBPC AFTER AGING 48 HOURS IN AIR AT 100°C

% DBPC Before Aging	Inherent Viscosity (dl/g)*
0.0	0.32
0.3	1.25
0.8	1.56
1.3	1.60
2.3	1.67

* After PIA to 250°C and 4 hours aging in Helium at 250°C.
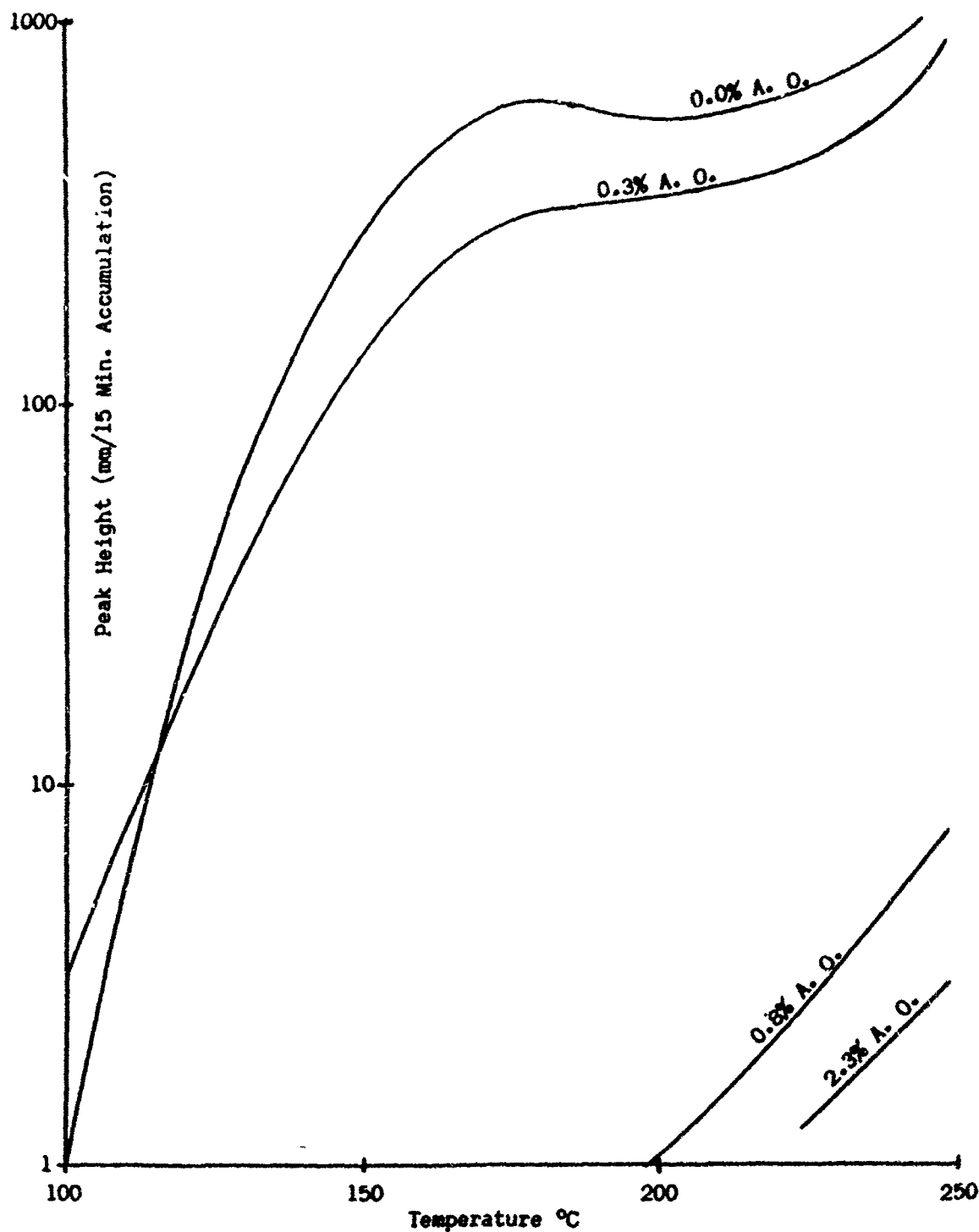
Figure 8. Evolution of Isobutene from Polyisobutene Containing
0 - 2.3% DBPC After 48 Hours Aging in Air at 100°C

19
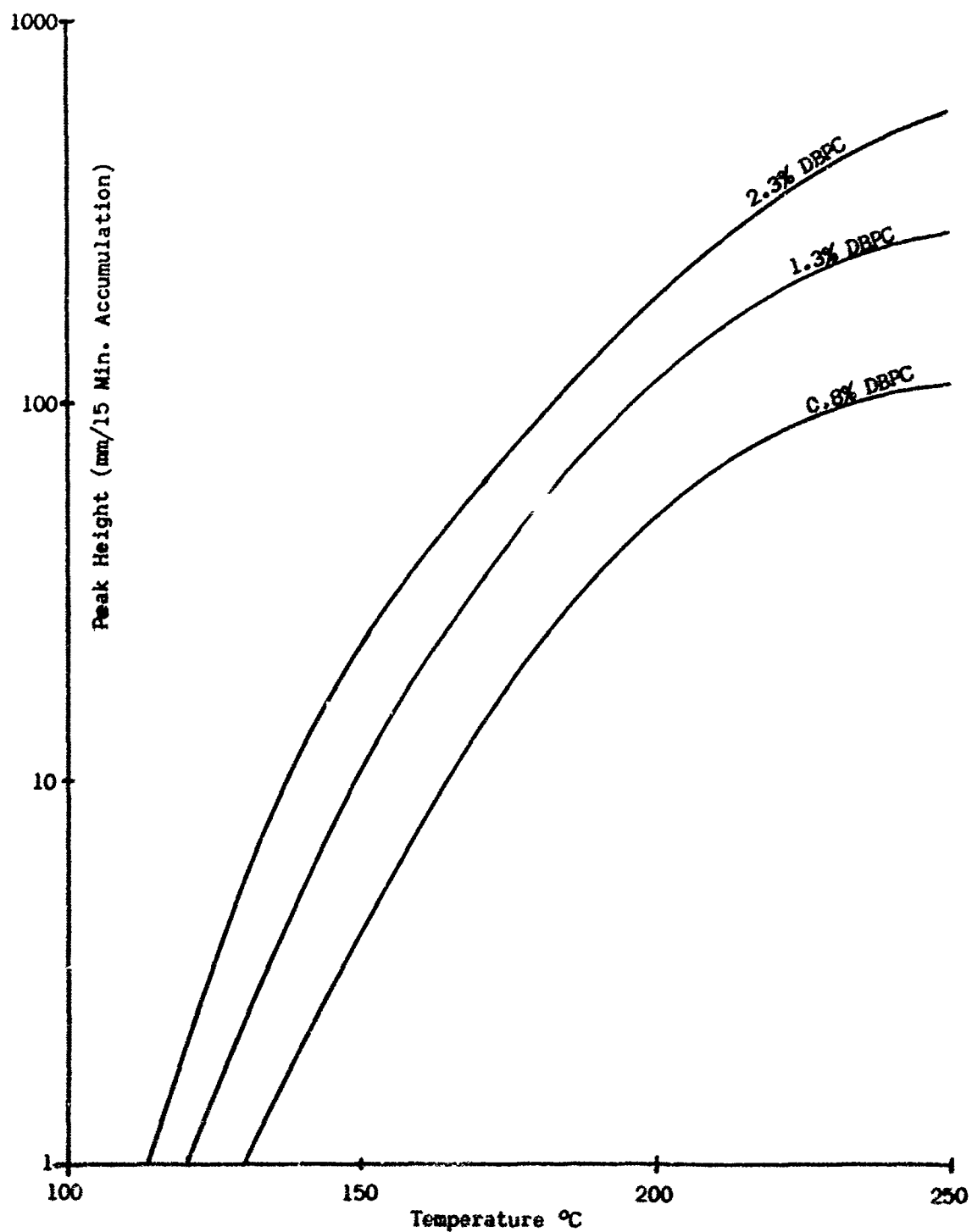
Figure 9. Evolution of Antioxidant from Unaged Polyisobutene
Containing 0.8 - 2.3% DBPC

20

cosities of these samples after PIA and additional aging are given in Table 3. These data also show that below the 0.8% DBPC level, a considerable drop in inherent viscosity is observed.

The thickness of the aged sample was found to be important in this study. Oven aging in air at 100°C had a much greater degrading effect upon thin samples than upon thick samples. It was found necessary to compare samples having nearly equivalent weight to surface ratios in order to obtain meaningful results.

The Effect of Molecular Weight on Degradation

The effect of molecular weight on thermal degradation was investigated. Polymers of two different average molecular weights 11,000 and 70,000, respectively, were subjected to PIA and air oven aging at 100°C followed by PIA. It was found that under similar conditions both polymers evolved degradation products in the same relative ratios. However, the low molecular weight polymer produced a greater quantity of volatiles during PIA both before and after oven aging. These results can be explained on the basis that there are proportionately a greater amount of activated sites present in the lower molecular weight polymer which are capable of initiating degradation.

Conclusions

The low temperature (up to 250°C) degradation mechanism indicated by the current investigations appears to be similar to the mechanism described previously by Simha, Wall and Blatz (2) with one exception. The initiation reaction to produce free radicals at these low temperature results from the decomposition of reactive sites along the polymer chain as proposed by Jellinek (3). Furthermore there appear to be three different types of reactive sites which decompose to initiate degradation.

The raw polymer will degrade slightly when heated above 200°C. Degradation is initiated by reactive sites already present in the polymer such as catalyst residues, branching, terminal unsaturation, etc. Antioxidant does not provide protection against this type of degradation.

The other two mechanisms of initiating degradation involve oxygen. Exposure of samples to oxygen when not protected by the presence of antioxidant results in the formation of oxygenated groups such as hydroperoxides along the polymer chain. The hydroperoxide groups are unstable at low temperatures and decompose to produce chain scission as described by Tobolsky (4). Depolymerization follows according to the theory of Simha, Wall and Blatz to produce quantities of isobutene. It has been found possible to decompose most of these hydroperoxide groups by heating polyisobutene to 175°C for 16 hours.

Oxidation also produces other oxygenated groups along the polymer chain which are more stable than hydroperoxides. It is necessary to heat samples above 200°C in order to initiate degradation resulting from the decomposition of the more stable oxygenated sites.

21

A polyisobutene with improved heat stability can be obtained if one uses a high molecular weight polymer whose naturally occurring reactive sites, which initiate degradation, can either be prevented or removed. Oxidative type attack can be minimized by using an efficient antioxidant which is not volatile at the aging temperature involved.

SECTION II

COMPOUNDING INVESTIGATIONS AND HIGH TEMPERATURE
PHYSICAL PROPERTIES OF ELASTOMERS

Compounding and testing activities under this contract were directed primarily at supplying vulcanizates having known physical properties for the thermal degradation and stress relaxation measurement portions of the program. These elastomers included butyl, polyisobutylene, ethylene-propylene, and silicone rubbers. No new commercial elastomers having promising high temperature resistance were encountered during the year. The new stress relaxation equipment was not completed in time to conduct measurements on all the compounds which follow.

BUTYL RUBBER

Resin cured butyl rubber is one of the better heat resistant materials that can be easily processed and which does not require postcuring operations. A series of compounds was prepared to illustrate the effect of carbon black level (0 to 100 phr) on the 400°F tensile strength of resin cured butyl as shown in Table 4. The 400°F tensile strength goes through a maximum at 80 phr HAF black in this formulation; however, when elongation is also considered, the 60 HAF compound (3064) would be preferred.

Using the 60 HAF resin cured butyl compound (3064) as a control, a second series of butyl compounds was mixed to compare several curing systems as shown in Table 5. Based on 400°F tensile strength, the resin cure was best, with three other compounds -- low sulfur and either TMTD (3068), or Tellurac plus Ethyl Cadmate (3069), and GMF, red lead, sulfur (3070) -- being about equal. GMF, red lead and MBTS (3071) produced a stock of lower tensile strength and elongation.

SILICONE RUBBER

Three samples of reclaimed silicone rubber (a potentially inexpensive heat resistant material which could be used alone or as a blending material) were obtained from the Xylos Rubber Company and were evaluated by curing with dichlorobenzoyl peroxide, dicumyl peroxide, and TDI Dimer. While the exact reclaiming procedure is not known, one sample was digested with rosin oil, one sample with formaldehyde, and one sample with a combination of both. All samples were gray, crumbly materials which sheeted well on the mill. The best properties were obtained with a dicumyl peroxide cure (7086) of the silicone rubber reclaimed with formaldehyde only (Table 6). The formaldehyde and any hydroxyl groups present were probably incidental to this curing system and had little interaction with the peroxide; whereas the rosin oil probably did react with the peroxides. The stocks containing TDI Dimer (diisocyanate) had very short elongations and tended to crumble in a manner suggesting gross overcure or polymer degradation. Points of attack for isocyanate crosslinking were possible hydroxyl groups attached to the reclaim after digestion with formaldehyde, or active hydrogen atoms.

Preparation of silicone reclaim without additives which would interfere with peroxide cures was suggested; however most of the oils presently added for satis-

TABLE 4

EFFECT OF CARBON BLACK LEVEL ON HIGH TEMPERATURE TENSILE STRENGTH OF RESIN CURED BUTYL

Base Compound: 100 Enjay Butyl 268, 5 Neoprene GRT, 5 zinc oxide, 3 zinc stearate, 3 Polar Oil 45, 0.02 magnesia, 10 CRR0803 resin.

Curing Temperature: 320°F

Stock No.		3061	3062	3063	3064	3065	3066
HAF Black		0	20	40	60	80	100
Stress-Strain Properties @ 73°F							
300% Modulus, psi							
Cure, min.	30	100	200	525	750	1425	1475
	45	75	250	600	950	1575	1675
	60	125	275	675	1100	1750	-
	90	75	300	750	1150	1800	-
Tensile Strength, psi							
Cure, min.	30	475	1675	2150	2000	1900	1475
	45	450	1675	2250	2025	1900	1675
	60	425	1800	2150	2100	2000	1575
	90	425	1900	2375	2100	2000	1575
Ultimate Elongation, %							
Cure, min.	30	780	840	760	680	420	300
	45	680	750	740	600	390	300
	60	680	770	660	580	360	270
	90	680	780	640	540	320	240
Stress-Strain Properties @ 400°F							
Tensile Strength, psi							
Cure, min.	30	50	100	460	670	770	630
	45	70	130	410	670	750	650
	60	60	110	430	590	830	650
	90	70	110	420	800	810	700
Ultimate Elongation, %							
Cure, min.	30	90	130	270	270	200	140
	45	140	180	220	260	180	140
	60	110	150	230	260	190	130
	90	130	160	200	280	200	130

TABLE 5

EFFECT OF CURE SYSTEM ON HIGH TEMPERATURE
TENSILE STRENGTH OF BUTYL COMPOUNDS

Base Compound: 100 Enjay Butyl 268, 60 HAF black, 5 zinc oxide, 3 Polar Oil 45.

Curing Temperature: 320°F

Stock No.	3064	3068	3069	3070	3071
Neoprene GRT	5	-	-	.	-
Zinc Stearate	3	-	-	-	-
Magnesia	0.02	-	-	-	-
Stearic Acid	-	1	1	1	1
CRR0803 Resin	10	-	-	-	-
Sulfur	-	0.5	0.5	1	-
GMF	-	-	-	2	1.5
Red Lead	-	-	-	-	5
MBTS	-	-	-	4	4
TMTD	-	3	-	-	-
Tellurac	-	-	1.5	-	-
Ethyl Cadmate	-	-	1.5	-	-

Stress-Strain Properties @ 73°F

		3064	3068	3069	3070	3071
300% Modulus, psi						
Cure, min.	30	800	1325	1175	1775	1900
	45	1000	1400	1125	2000	1925
	60	1150	1375	1050	2075	1725
	90	1250	1400	1075	2125	1850
Tensile Strength, psi						
Cure, min.	30	2025	2075	2200	2300	2075
	45	2075	2225	2125	2525	2000
	60	2125	2125	2050	2475	1725
	90	2150	2200	2100	2425	1850
Ultimate Elongation, %						
Cure, min.	30	640	500	530	430	320
	45	620	480	520	420	310
	60	580	470	520	380	300
	90	500	480	520	340	300

Stress-Strain Properties @ 400°F

		3064	3068	3069	3070	3071
Tensile Strength, psi						
Cure, min.	30	710	600	670	620	480
	45	780	640	690	660	410
	60	800	640	630	650	410
	90	820	640	650	630	410
Ultimate Elongation, %						
Cure, min.	30	320	490	570	290	170
	45	270	460	560	270	160
	60	280	460	470	260	160
	90	270	450	450	250	160

TABLE 6

EVALUATION OF RECLAIMED SILICONE RUBBER

Base Compound: A = silicone rubber reclaimed with rosin oil and formaldehyde
B = silicone rubber reclaimed with rosin oil only
C = silicone rubber reclaimed with formaldehyde only

Stock No.	7081	7082	7083	7084	7085	7086	7087	7088	7089
Silicone Reclaim A	100	100	-	-	-	-	100	-	-
Silicone Reclaim B	-	-	100	100	-	-	-	100	-
Silicone Reclaim C	-	-	-	-	100	100	-	-	100
Hi-Sil 233	4	4	4	4	4	4	4	4	4
Dichlorobenzoyl Peroxide (40%)	1.25	-	1.25	-	1.25	-	-	-	-
Dicumyl Peroxide (40%)	-	1	-	1	-	1	-	-	-
TDI Dimer	-	-	-	-	-	-	10	10	10
Curing Temperatures									
Press Cure, min./°F	10/250	10/320	10/250	10/320	10/250	10/320	15/300	15/300	15/300
	All stocks postcured 4 hours @ 400°F in oven.								
Stress-Strain Properties @ 73°F									
Tensile Strength, psi	50	75	175	100	350	500	25	50	200
Ultimate Elongation, %	40	50	140	50	130	150	40	20	40
Shore 'A' Hardness	53	54	49	53	61	64	crumbled blocks		

factory processing on reclaiming equipment will interfere with the commonly used peroxides. Silicone reclaims with other additives were not obtained during the contract period.

ETHYLENE-PROPYLENE RUBBERS

Ethylene-propylene copolymer rubber (EPR) cured with sulfur and peroxide and containing the stabilizing agents antimony trioxide and chlorosulfonated polyethylene (Hypalon) had good resistance to heat aging at 350 - 400°F (25). Ethylene-propylene terpolymers (EPT) containing small amounts of unsaturation have now become available which are susceptible to resin cures of the type used in heat resistant butyl rubber compounds. The resin cure, the stabilizing agents, and variations in mixing procedure were combined in the evaluation of one series of EPT compounds.

Resin cured EPT (Enjay 3509) compounds were mixed two ways to determine the effect of adding the activator ($SnCl_2 \cdot 2H_2O$) and stabilizing agents in the masterbatch (stocks 7091, 7092) instead of in the final mix (stocks 7094, 7095). The results in Table 7 indicate that addition of these agents to the masterbatch (Base Compound A) raised the viscosity of the uncured stocks, and reduced the modulus, tensile strength, and hardness of the vulcanizates slightly. All four vulcanizates shown were tightly cured initially and had undesirably short elongations at 400°F and at 73°F after aging at 400°F. Tensile strength at 400°F and resistance to aging at 400°F were essentially equal for the two types of mixing. Apparently the longer interaction of $SnCl_2 \cdot 2H_2O$ with the polymer when added in the masterbatch does not result in increased beneficial crosslinking.

A resin cured EPT compound utilizing SAF black and having a Shore A hardness of 70 was submitted for stress relaxation measurements to illustrate the capabilities of the new stress relaxation equipment built under this contract. The stress-strain properties of this compound measured at 73 and 400°F are shown in Table 8.

27

TABLE 7

RESIN CURES OF ETHYLENE-PROPYLENE TERPOLYMER RUBBER

Base Compound A: 100 Enjay 3509, 10 polyisobutene, 50 HAF black, 2 $SnCl_2 \cdot 2H_2O$ (75%), 5 Hypalon 20, 5 antimony trioxide.

Base Compound B: 100 Enjay 3509, 10 polyisobutene, 50 HAF black.

Curing Temperature: 320°F

Stock No.	7091	7092	7094	7095
Base Compound A	172	172	-	-
Base Compound B	-	-	160	160
Hypalon 20	-	-	5	5
Antimony Trioxide	-	-	5	5
$SnCl_2 \cdot 2H_2O$ (75%)	-	-	2	2
CRR0803 resin	8	-	8	-
SP1055 resin	-	8	-	8

Mooney Viscosity @ 265°F

	7091	7092	7094	7095
Minimum	62	67	55	55

Stress-Strain Properties @ 73°F

300% Modulus, psi

Cure, min.		7091	7092	7094	7095
	30	2100	-	2400	-
	60	2150	-	2600	-
	90	2200	-	-	-

Tensile Strength, psi

Cure, min.		7091	7092	7094	7095
	30	2325	1975	2400	2050
	60	2150	2200	2450	2175
	90	2200	2150	2200	2275

Ultimate Elongation, %

Cure, min.		7091	7092	7094	7095
	30	320	260	300	240
	60	300	260	280	220
	90	300	260	260	220

Stress-Strain Properties @ 400°F

Tensile Strength, psi

Cure, min.		7091	7092	7094	7095
	30	430	370	450	380
	60	420	480	500	480
	90	430	400	415	510

Ultimate Elongation, %

Cure, min.		7091	7092	7094	7095
	30	100	60	80	70
	60	100	90	90	80
	90	80	70	80	80

TABLE 7 (CONT'D)

Stock No.	7091	7092	7094	7095
Stress-Strain Properties @ 73°F After Aging 8 Hours @ 400°F				
Tensile Strength, psi				
Cure, min.　30	675	775	600	650
60	625	750	500	650
90	575	750	525	700
Ultimate Elongation, %				
Cure, min.　30	110	100	80	70
60	110	90	70	70
90	110	100	70	70
Shore 'A' Hardness - Cured 75 min.				
Normal	66	69	68	71
Aged 8 hrs. @ 400°F	72	73	75	78

TABLE 8

STRESS-STRAIN PROPERTIES OF EPT COMPOUND
USED IN STRESS RELAXATION MEASUREMENTS

Stock No. 3294:   100 Enjay 3509, 5 Hypalon 20, 10 polyisobutene, 55 SAF black, 5 Flexon 765, 5 antimony trioxide, 8 CRR0803 resin, 2 $SnCl_2 \cdot 2H_2O$ (75%).

Curing Temperature: 320°F

		73	400	73
Test Temperature, °F:		73	400	73
Aged 8 Hours @ °F:		-	-	400

Stress-Strain Properties

Tensile Strength, psi					
Cure, min.	30		2000	370	650
	45		1900	350	700
	60		1725	350	700
Ultimate Elongation, %					
Cure, min.	30		250	60	60
	45		230	60	70
	60		200	50	70

Shore 'A' Hardness		70	-	-

SECTION III

STRESS RELAXATION APPARATUS

The high vacuum, high temperature stress relaxation apparatus has been completed and tests have been run in order to check its operation and to make certain that the apparatus meets the specifications which were set up for it (Table 9). These tests have shown that the apparatus is perfectly satisfactory and that it meets or exceeds the specifications. An invention disclosure is being filed on the apparatus.

DESCRIPTION OF THE APPARATUS

The apparatus consists essentially of a stainless steel, electrically heated oven connected to a high vacuum system comprised mainly of mechanical and oil diffusion pumps with associated valves and manifold. Inside the oven there are two sample holders, one of which (the fixed holder) is attached to the end of a beam mounted on monoflexures, while the other (the moveable one) is fastened to the end of a bellows-sealed rod which extends outside the oven. The latter holder can be moved in a vertical path by means of a handwheel which operates a rack and pinion drive to the rod. The fixed holder attached to one end of the beam transmits the force exerted by the elastomeric sample to the beam where it is in turn transferred to the load cell located at the other end of the beam. The manufacturer's specifications for the load cell are given in Table 10. The ring shaped sample is hooked over small rollers on the ends of the two holders. By the above means, the sample can be elongated at any desired time while under reduced pressure by turning the handwheel. The electrical analog of the force exerted by the sample is recorded continuously on a strip chart recorder whose input is the output from the load cell. The amplitude of the recorder trace is proportional to the force on the sample.

The input and output leads of the load cell and also the leads from 3 thermocouples are lead into the evacuated space through two glass sealed multilead electrical feed-throughs. One thermocouple monitors the temperature of the load cell while the other two are used for measuring the temperature in the oven in the immediate vicinity of the sample.

It is believed that this apparatus is unique in that the load cell is located within the evacuated space. Many types of tensile testers, relaxation devices, etc., have been made which employed a load cell for measuring forces, but in every case we are aware of, the load cell located outside the heated or evacuated space -- this means that these devices all have some way of sealing the rod (or whatever was used) used to transmit the force from the inside to the outside of the enclosed space. Any type of seal results in variable frictional forces which destroy sensitivity and accuracy. This apparatus employs a standard load cell without special modifications (such as liquid cooling).

Another unusual feature of the apparatus is the absence of any rotating or sliding seals or bearings. There are no parts in the relaxation apparatus itself which employ materials in contact with relative motion with the exception of the small rollers for holding the sample. This eliminates many problems such as wear,

TABLE 9

SPECIFICATIONS FOR APPARATUS

temperature range	room temperature to 500°F
load capacity	0 to 25 pounds
overload	50% (150% of rated capacity)
sensitivity (normal)	about .03 pounds can be read directly with 10 volts into load cell, a 1 to 1 ratio on beam and a 0 - 5 mv recorder
(maximum)	about .0075 pounds with 20 volt input, lever ratio on beam of 2 to 1, and a 0 - 5 mv recorder - maximum load 12.5 pounds
normal vacuum during test	2×10^{-5} to 7×10^{-5} mm Hg
pump down time	varies from 1/2 hour to 1-1/2 hours depending on sample, etc.
stress range (with ring shaped sample of .22 x .075" section)	0 to 760 psi - can be extended to about 0 to 1500 psi by using narrower sample
elongation range	0 to 350% (total stroke of about 6")

facilities required:

main source of electrical power	120/208 3 phase, 20 ampere A-C outlet with 4 prong receptacle
load cell supply	0 - 20 volt adjustable D. C. supply with filtered output, regulation and voltmeter
water	approximately 1/4 gal./min. of 50 - 68°F input and drain

32

TABLE 10

MANUFACTURER'S SPECIFICATIONS FOR LOAD CELL

rated capacity	25 pounds
maximum load	50% overload (150% of rated capacity)
maximum input voltage	20 volts D. C. or A. C. RMS
compensated temperature range	30°F to 150°F
maximum temperature range	-50°F to 200°F
effect of temperature on zero	± .002% of rated capacity per °F
effect of temperature on output	± .002% of reading per °F
linearity	± .1% or rated capacity
output in compression	2.13 mv/volt at rated capacity

The load cell has been used with 10.0 volts D. C. input. See conversions below:

10 volts input at 2.13 mv/volt = 21.3 mv for 25 pounds

1 lb. = 21.3/25 = .852 mv

1 mv = 25/21.3 = 1.174 lb.

33

lubrication, leaks due to worn seals, etc. The mounting "pivot" of the beam is of the mono-flexure type which completely eliminates ordinary friction. It is sensitive and has large load carrying capacity and requires no lubrication or care except to see that it is not overloaded or roughly handled. The beam flexure (pivot point) is set in the center of the beam, giving a 1 to 1 ratio for the beam. The pivot point can be moved to give a 2 to 1 ratio for greater sensitivity (with decreased load capacity). Moving the pivot point must be done with oven opened to atmospheric pressure. Extreme caution is necessary when making any adjustments to the beam. Although the flexures will take any load up to the maximum given in the specifications without damage, they can easily be damaged by twisting or flexing the beam beyond the elastic limit of the flexures.

All seals in the relaxation apparatus proper are of the static type. These seals include a number of Viton "O" rings and several glass-to-metal seals. All parts in the evacuated, heated area are of stainless steel or glass. Valves in the vacuum system are of the bellows sealed type with the exception of the large gate valve at the top of the diffusion pump. This gate valve is the only part employing seals which are of the relative motion type. Photographs of the apparatus are shown in Figures 10, 11, and 12.

In general the apparatus has proven to be very satisfactory. The temperature and pressure specifications originally set forth were easily met and there appear to be no difficult or critical characteristics. The tests did show up the possibilities of minor improvements for ease of testing such as the desired addition of a leak valve in the oven so that samples could be changed without letting air into the manifold and pumps. Although the use of a load cell in an evacuated, heated space had caused some apprehension, the tests so far have turned up no difficulties in this respect. The load cell temperature was only 86°F in the 500°F test and there has been no trouble outgassing the oven in the 10^{-5} mm range. Because of the very limited amount of experience with this equipment the following discussion of its characteristics and limitations is presented in some detail.

TYPES OF TESTS WHICH CAN BE MADE

In general, three types of tests associated with relaxation have been in common use:

1. Continuous stress relaxation tests in which the sample is elongated to a predetermined length and then held at this length while readings of the relaxing force are taken.

2. Intermittent stress relaxation tests in which the sample is put under cycles of elongation and free relaxation with force measurements being made periodically during the test.

3. Creep tests in which the sample is elongated by a constant load and periodic measurements of length of the sample are made.

The apparatus described in this report is capable of continuous or intermittent stress relaxation tests on ring shaped samples. Creep tests could be made if
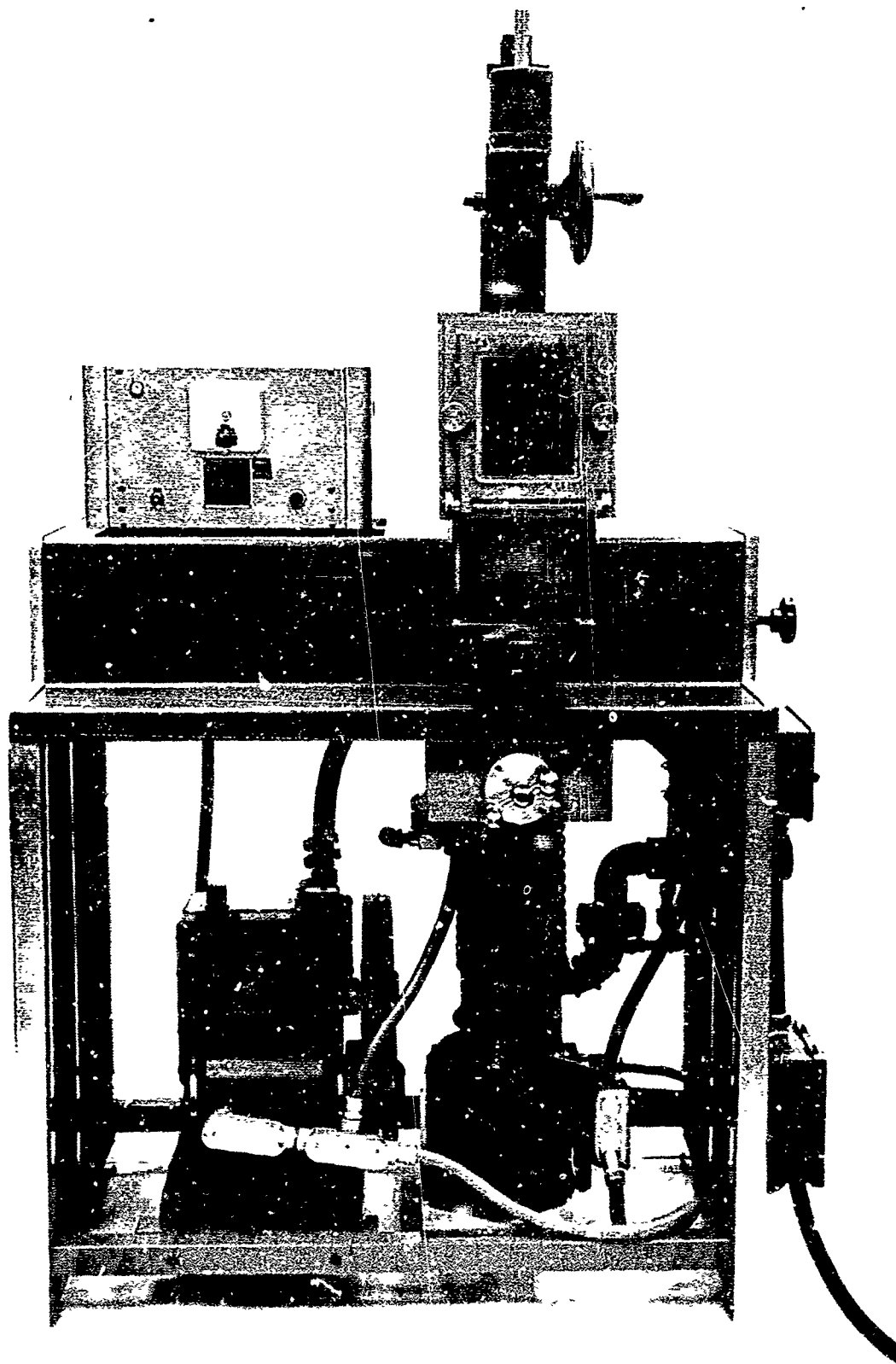
34

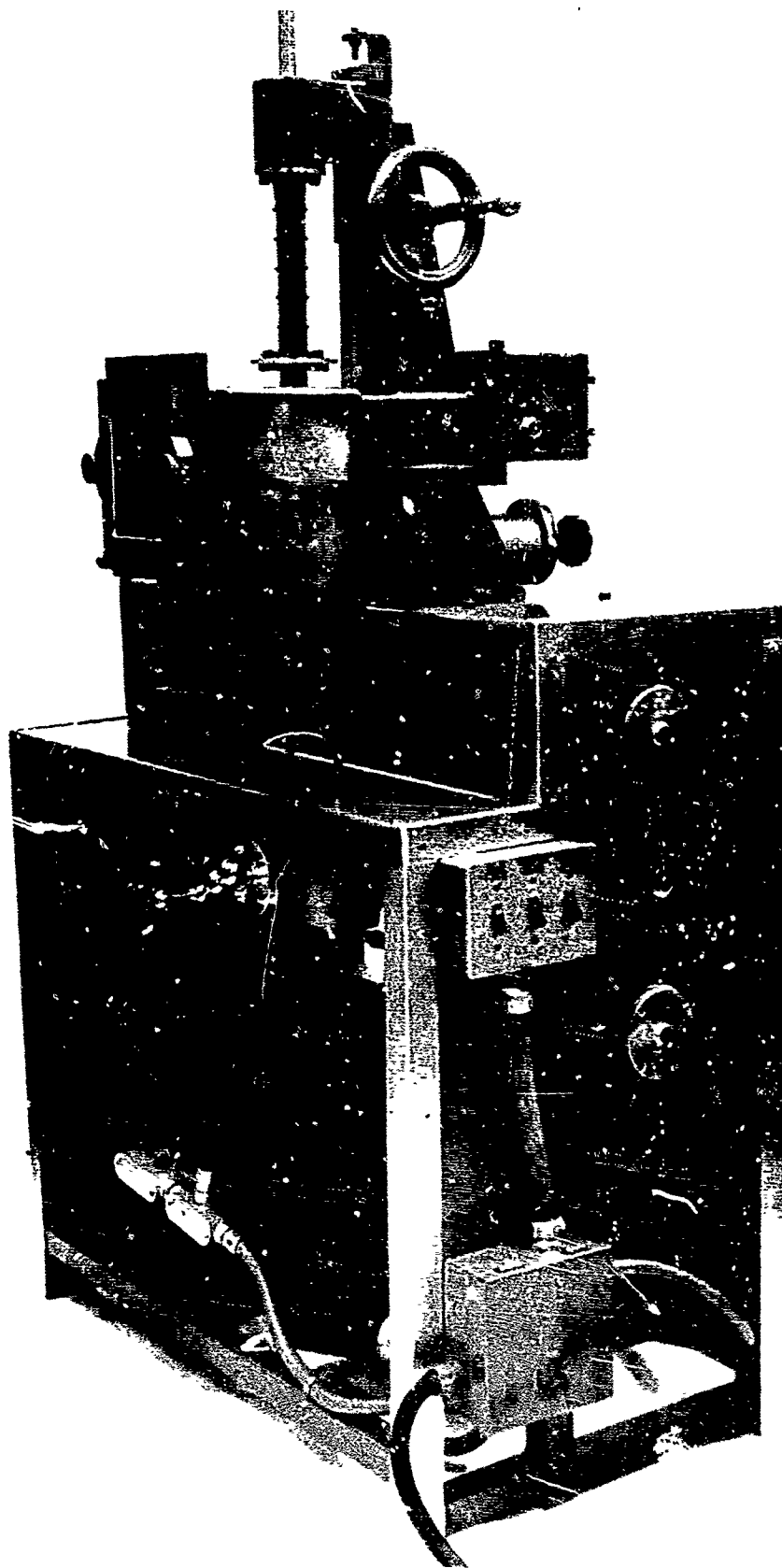Figure 10. Stress Relaxometer -- Front View
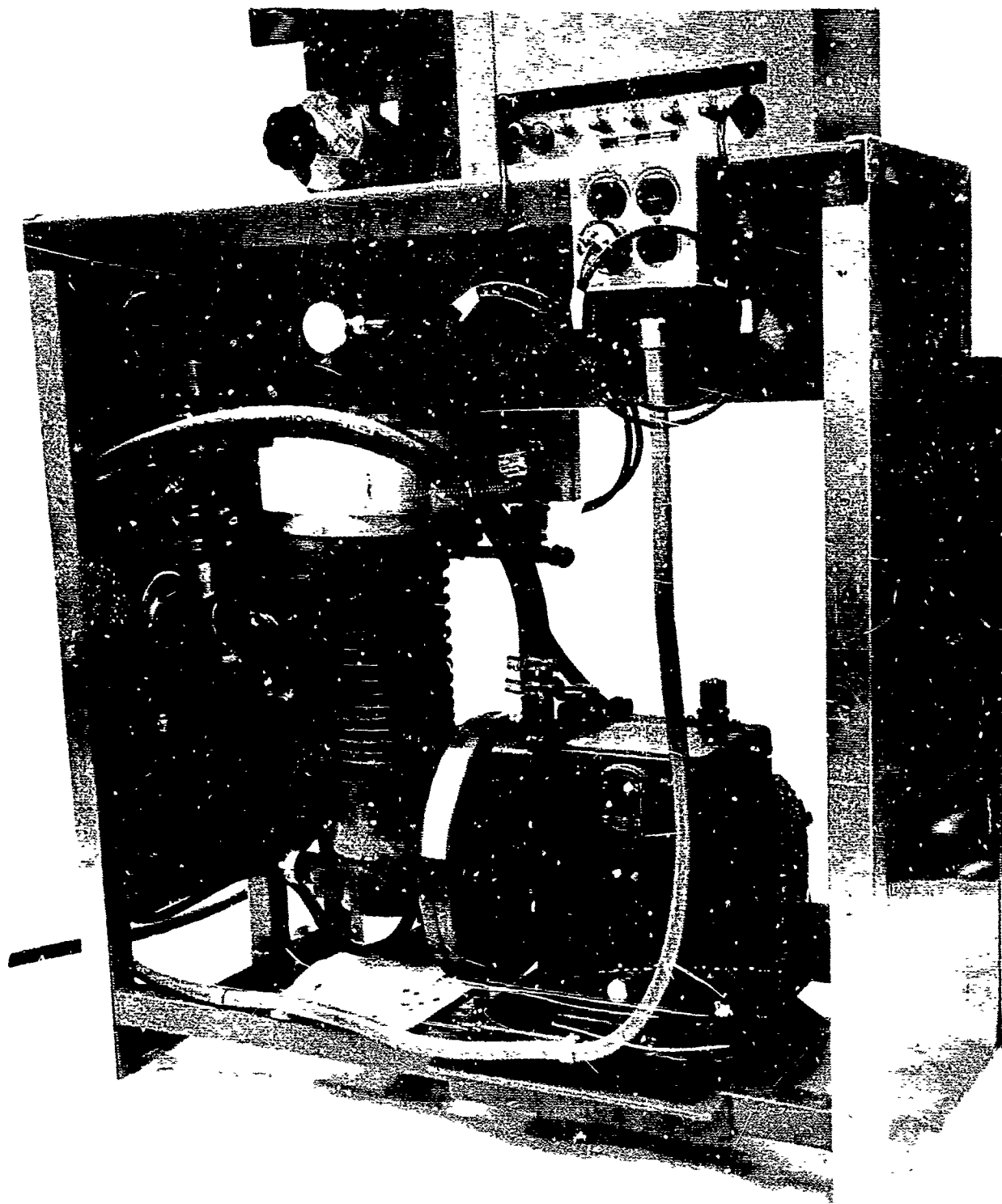
35

Figure 11. Stress Relaxometer -- Right Side View

Figure 12. Stress Relaxometer -- Rear View

necessary by periodically re-adjusting the elongation of the sample by means of the hand wheel in such a manner that the load is kept constant as indicated by strip chart recorder. The changing length of the sample would be measured by the motion of the slide on the rack and pinion drive.

As set up, the apparatus can not be used with static or dynamic air or inert gas atmo   · as was originally planned before the vacuum test was suggested. However   .ications to include dynamic inert gas testing have been planned and will re. ..e only the addition of two leak valves of the needle type plus a gas regulator/gage combination to meter the gas. As furnished, the apparatus is to be used for vacuum tests only.

MEASUREMENTS OF PRESSURE IN OVEN

To date, the apparatus has been used in conjunction with a glass McLeod gage made at this laboratory by Dr. J. L. Binder and Mr. E. C. Stair. The McLeod gage and an associated glass vacuum system were made to calibrate the Phillips type ionization gage loaned to us by the Government for this project. The ionization gage could not be repaired and calibrated satisfactorily. Because of this, the McLeod gage has been used in all tests. The latter gage is accurate and will read directly to 1×10^{-6} mm Hg but is very inconvenient to use. The pump down time is shown in Figure 13.

DESIRABLE MODIFICATIONS OF APPARATUS

1. The ionization gage should be repaired by the factory or a new gage obtained. The use of the McLeod gage is inconvenient and makes leak testing very difficult because one cannot obtain continuous pressure readings with it. The stress relaxation apparatus still has small leaks as shown by the rise of pressure of the system when valved off from the pumps. These leaks could be located if a continuous reading pressure gage were available.
    Note: The pressure can be reduced to the low 10^{-5} mm range in spite of the leaks, but with a tighter system would probably go to the 10^{-6} or 10^{-7} mm Hg range.

2. Addition of leak valve to oven.

3. At present, the heaters in the oven are controlled by means of a manually adjusted Variac -- the addition of an automatic temperature control would be a highly desirable feature for any extensive testing.

4. Addition of a regulated low power D. C. source for the load cell input. Batteries could be used if of adequate capacity. At present a low cost D. C. source is being used but it is not regulated   inaccuracy.

TEMPERATURE CHECKS ON APPARATUS

During the 500°F tests, temperatures of the outside of various parts of the apparatus were measured. These are as follows: glass in door 230°F, left side
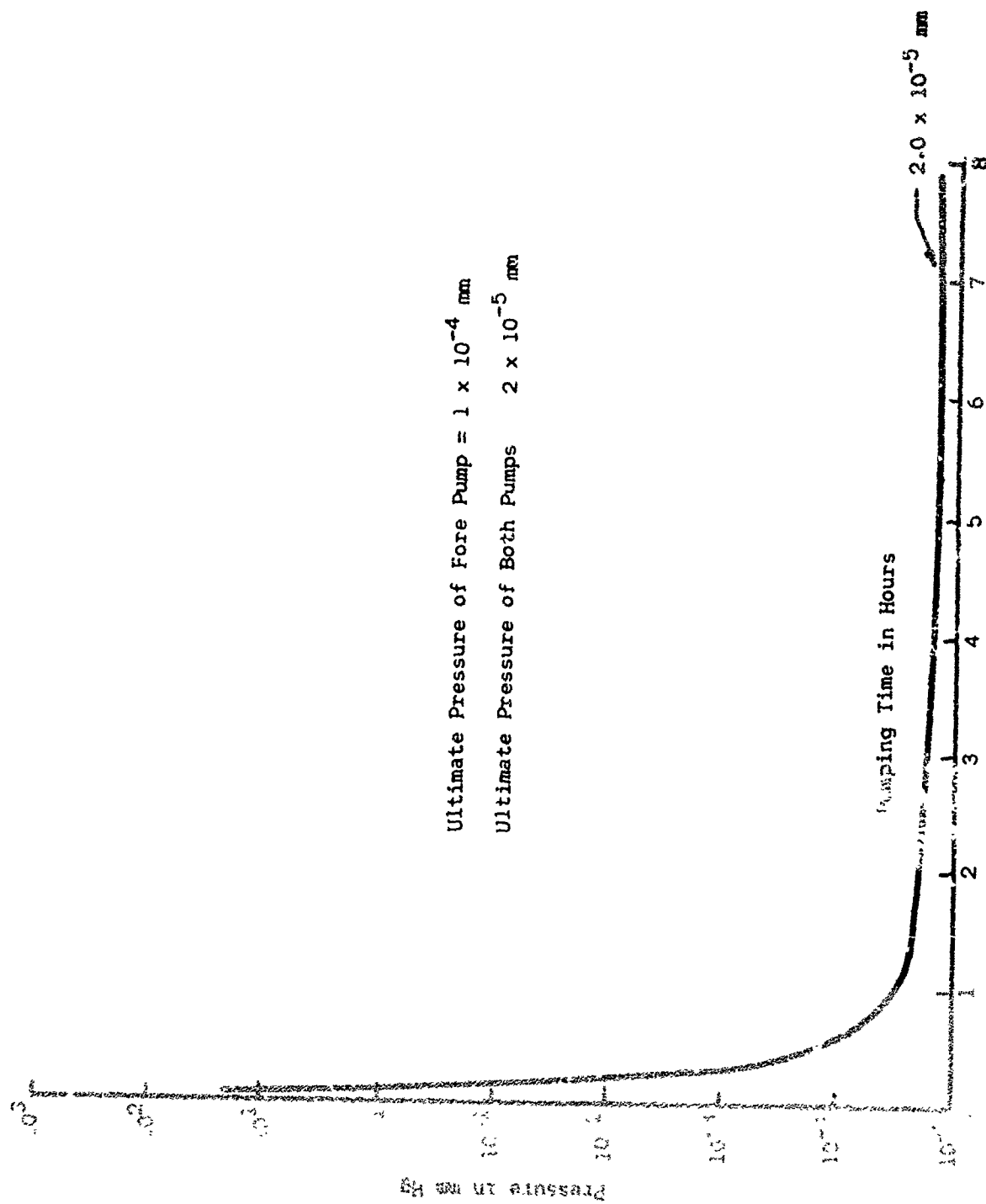
Ultimate Pressure of Fore Pump = 1×10^{-4} mm

Ultimate Pressure of Both Pumps = 2×10^{-5} mm

2.0×10^{-5} mm

Pumping Time in Hours

Pressure in mm Hg

Figure 13. Pressure vs Pump Down Time

39

of oven 235°F, top of oven 195°F, bottom 185°F, door flange near seal 150°F, top flange near seal 126°F, load cell 86°F (inside oven).

SAMPLE SIZE AND CURING

The sample used is a ring shaped sample 1.10 inch I. D. x 0.21 inch wide x 0.075 inch thick. It is made by first curing rubber in a transfer type mold which results in a cylinder about 5 inches long. The cylinder is then mounted on a wooden mandrel and the assembly is rotated in a lathe while rings are cut from the cylinder by means of two single edged razor blades mounted 0.21 inch apart in a fixed holder mounted in the lathe tool post.

This sample is not the best shape one could choose for ease of making but was chosen because the ring shaped sample is easy to hold in the oven; i.e. it does not require clamps as a dumbell strip would.

SETTING OF THE SAMPLE HOLDERS

The sample holders are set at a roller center-to-center distance of 1.20" for 0% elongation and 2.09" for 50% elongation. Table 11 gives settings for other elongations.

It should be noted that there are two stops on the stroke of the dove tail slide. The lower stop is fixed and is set to limit the compression of the bellows. The upper stop is adjustable but has been set to give a 1.20" center-to-center distance for the rollers. If this stop is changed, care must be taken to adjust to a point where the slide will be stopped before the moveable holder touches the fixed holder, otherwise the beam flexure might be damaged. In any case the bellows should not be extended beyond 7.8" total length.

40

TABLE 11

SETTINGS FOR ELONGATIONS DESIRED

Elongation %	Roller Separation* inches	Inner Periphery of Sample inches	Scale Reading** inches
0	1.20	3.58	0.0
50	2.09	5.37	.89
100	2.99	7.16	1.79
150	3.88	9.95	2.68
200	4.78	10.74	3.58
250	5.67	12.53	4.47
300	6.57	14.32	5.37
350	7.46	16.11	6.26

*   Center-to-center distance of rollers.

**   With scale set at 0% elongation = 0 inches.
Note: These figures have been calculated using a roller separation (1.20")
just sufficient to straighten out the sample for 0% elongation and a sample
size of 1.10" I. D.

41

RESULTS OF TESTS

Curves of stress vs. time at temperatures of 100, 400 and 450°F for a resin cured butyl stock (No. 3064) have been plotted as an example of continuous stress relaxation tests in Figure 14. These curves have been adjusted to start at the same initial stress for easier comparison of the relative slopes. It should be noted that the actual stress on individual samples differ, but that in this test the important thing is the rate of decay, that is, the slope of the curves. Normally, the tests are run for a time sufficient to cause the stress to relax 63.2% of the .5 minute stress. These tests were abbreviated to 360 minutes or less because of time limitations. A 500°F test is not shown because the sample broke immediately upon loading.

Figure 15 gives stress relaxation curves for stock No. 3064 when tested at 200°F in a vacuum at 200°F in air in the same apparatus, and at 248°F in air in the regular Firestone apparatus. These tests indicate that there is a significant difference in the decay rate at 200°F between the vacuum and air tests in the same apparatus. This effect, is of course, the raison' d'etre for the vacuum test.

Although one can draw no conclusions from one test, the result is satisfying in that it is "the right direction".

The 248°F test was conducted in air in the regular Firestone stress relaxation test apparatus (26). It is included for comparison of results in the two pieces of apparatus. The curves have again been adjusted to start at the same stress.

Figure 16 compares the relaxation of an EPT stock (No. 3294) in vacuum and in air. These curves show quite vividly the difference in vacuum and air tests. At the start of the testing period, the rates of relaxation are similar, and there is not much difference until after about 30 minutes. From then on, the vacuum sample continues to relax in a manner that appears to be linear with log time, while the air sample drops off sharply in stress. At the end of the test the vacuum sample stress is about 205 psi while the air sample stress is only about 70 psi. Allowing for the differences in the original stresses, the test ends with the vacuum sample at a stress over 2½ times that of the air sample.

It is apparent that the rates of decay are nearly alike at the start but progressively differ more and more as time increases. This appears to be due to the fact that oxygen has little time to act at first, but soon starts degrading the air sample.
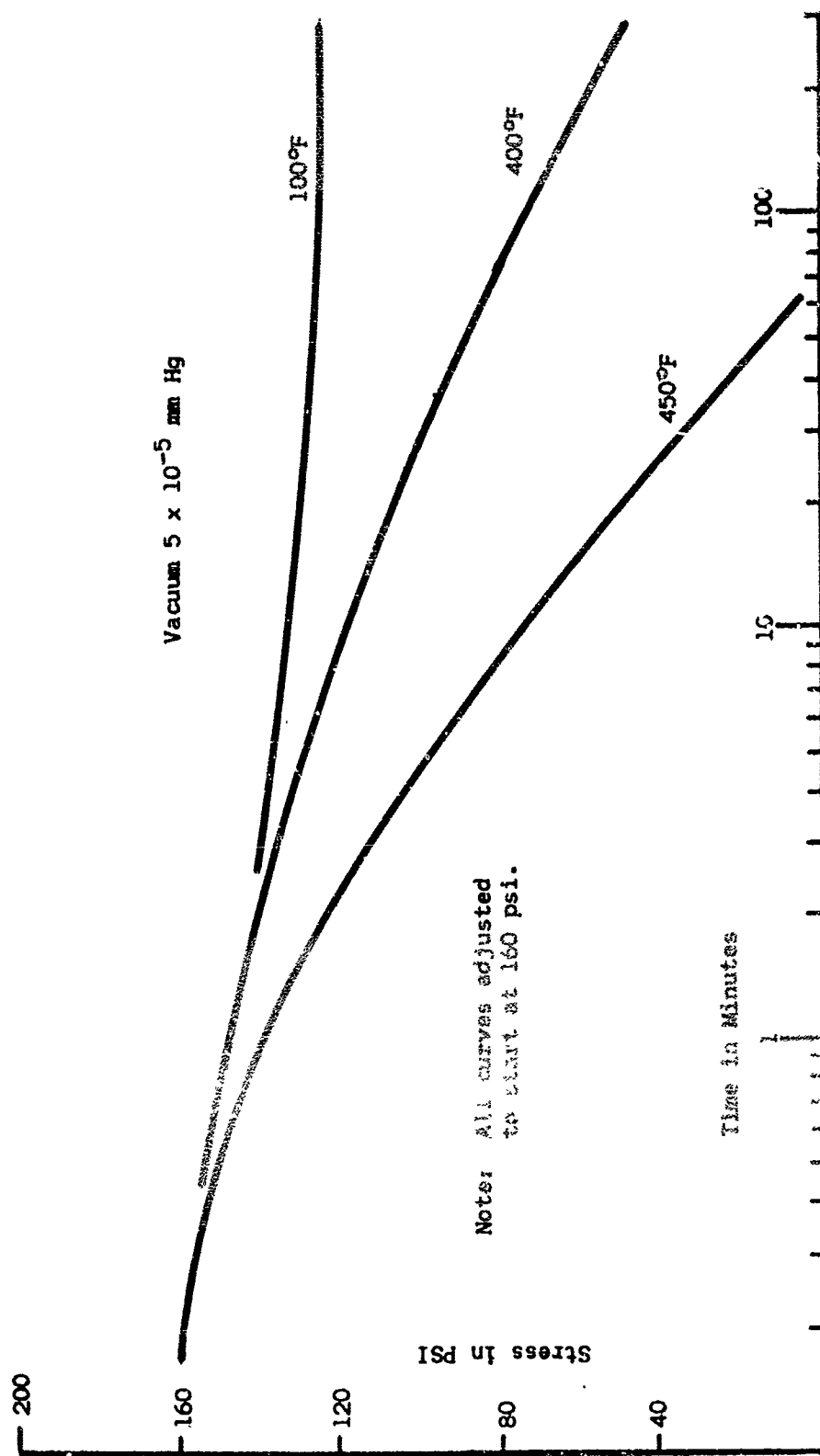
42

Figure 14. Continuous Stress Relaxation of Resin Cured Butyl Stock No. 3064
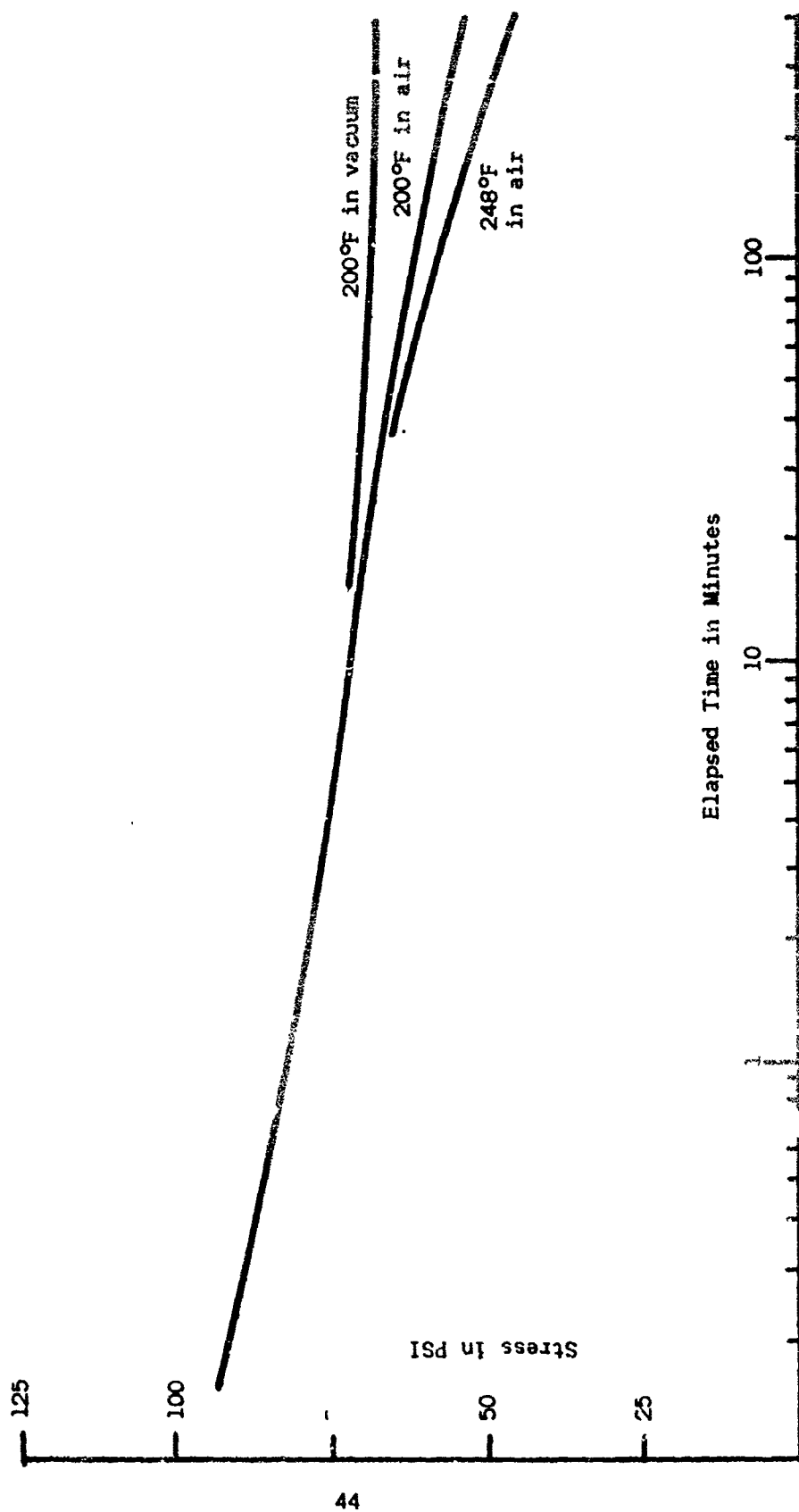
43

Figure 15. Continuous Stress Relaxation of Resin Cured Butyl Stock No. 3064 at 50% Elongation
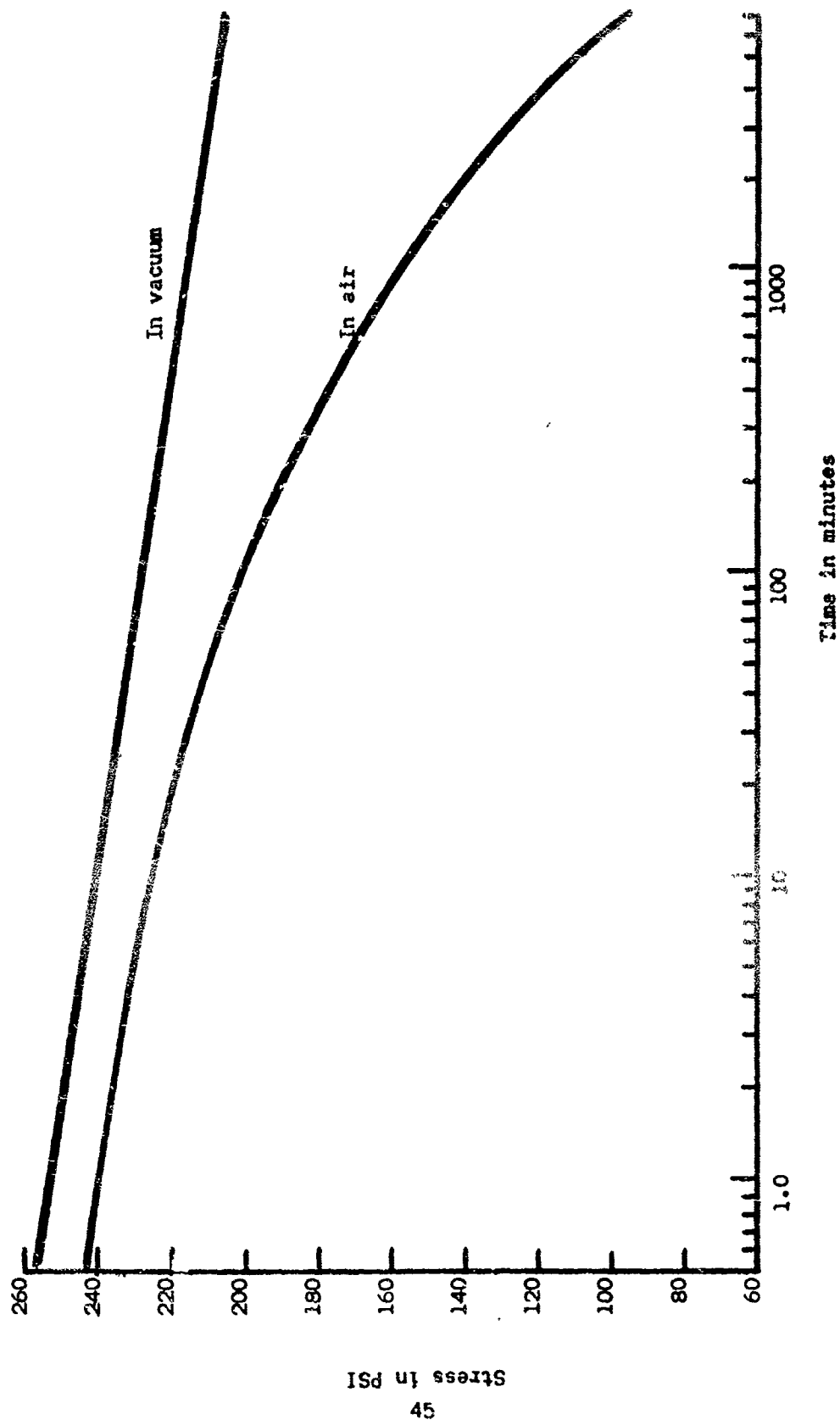
44

Figure 15. Continuous stress relaxation of EPT at 300°F - stock 3294
Elongation 50% - ring shaped sample

45

REFERENCES

1. Madorsky, S. L., Straus, S., Thompson, D., and Williamson, L., *J. Poly. Sci.* 4, 639 (1949).

2. Simha, R., Wall, L. A., and Blatz, P. J., *J. Poly. Sci.* 5, 615 (1950).

3. Jellinek, H. H. G., "High Temperature Resistance and Thermal Degradation of Polymers", S. C. I. Monograph No. 13, Macmillan Co., N. Y., 1961, p. 1.

4. Tobolsky, A. V., Metz, D. J., and Mesrobean, R. B., J.A.C.S. 72, 1942 (1950).

5. Wall, L. A. and Florin, R. E., *J. Research Natl. Bur. Standards* 60, 451 (1958).

6. Wall, L. A., "High Temperature Resistance and Thermal Degradation of Polymers", S. C. I. Monograph No. 13, Macmillan Co., N. Y., 1961, p. 146.

7. Schooten, J. V. and Wijga, P. W. O., "High Temperature Resistance and Thermal Degradation of Polymers", S. C. I. Monograph No. 13, Macmillan Co., N. Y., 1961, p. 432.

8. High Temperature Elastomer Compounds Technical Documentary Report ML TDR 64-30, January 1964, p. 2.

BIBLIOGRAPHY

Thermal Decomposition of Polymers

1. Achhammer, B. G., Reinhart, F. W. and Kline, G. M., J. Research Natl. Bur. Standards 46, 327 (1953)

2. Druesedow, D. and Gibbs, C. F., "Polymer Degradation Mechanisms", Natl. Bur. Standards Circular No. 525, 1953 p. 69.

3. Gaeta, L. J., J. C. Henning, F. M. Smith, J. D. Rigby, G. L. Hall, M. C. Thorckmorton, and M. J. Brock, High Temperature Resistant Elast... Compounds. WADC Technical Documentary Report 56-331, Part VII. Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. January 1963, p. 107.

4. Grassie, N., "Chemistry of Vinyl Polymer Degradation Processes", Butterworths, London, 1956.

5. High Temperature Elastomer Compounds Technical Documentary Report ML TDR 64-30 January 1964, p. 2.

6. Jellinek, H. H. G., "High Temperature Resistance and Thermal Degradation of Polymers", S. C. I. Monograph No. 13, Macmillan Co., N. Y., 1961, p. 1.

7. Jellinek, H. H. G., "Degradation of Vinyl Polymers", Academic Press, New York, 1955.

8. Jellinek, H. H. G., Natl. Bur. Standards, Circular No. 525, 1953, p. 1.

9. Madorsky, S. L., Straus, S., Thompson, D., and Williamson, L., J. Poly. Sci. 4, 639 (1949).

10. Madorsky, S. L., J. Polymer Sci. 11, 491 (1953).

11. Oakes, W. G. and R. hards, R. B., J. Chem. Soc. (1949) 2929.

12. Schooten, J. V. and Wijga, P. W. O., "High Temperature Resistance and Thermal Degradation of Polymers", S. C. I. Monograph No. 13, Macmillan Co., N. Y., 1961, p. 432.

13. Simha, R., "Degradation of Polymers", Advances in Chemistry Series, No. 34, p. 157 (1962).

14. Simha, R., "Mechanisms and Kinetics of Chain Degradation", "Proceedings of the International Symposium on Macromolecular Chemistry", Pergamon Press, New York, 1957, p. 250.

15. Simha, R., and Wall, L. A., J. Poly. Sci. 6, 39 (1951).

16. Simha, R., and Wall, L. A., J. Phys. Chem. 56, 707 (1952).

BIBLIOGRAPHY (CONT'D)

17. Simha, R., Wall, L. A., and Blatz, P. J., _J. Poly. Sci._ 5, 615 (1950).

18. Tobolsky, A. V., Metz, D. J., and Mesrobean, R. B., J.A.C.S. 72, 1942 (1950).

19. Tobolsky, A. V., Prettyman, I. B., and Dillon, J. H., _J. Applied Physics_ 15, No. 4, 380 - 395 (1944).

20. Wall, L. A., "Pyrolysis", "Polymer Analysis", Chapter 5, Editor, G. M. Kline, Interscience, New York, 1962.

21. Wall, L. A., "High Temperature Resistance and Thermal Degradation of Polymers", S. C. I. Monograph No. 13, Macmillan Co., N. Y., 1961, p. 146.

22. Wall, L. A., _SPE Journal_ 16, 810 (1960).

23. Wall, L. A., "Polymer Degradation Mechanisms", Natl. Bur. Standards Circular No. 525, 1953, p. 239.

24. Wall, L. A. and Florin, R. E., _J. Research Natl. Bur. Standards_ 60, 451 (1958).

25. Wall, L. A. and Flynn, J. H., _Rubber Chem. and Tech._ 35, 1157 (1962).

26. Wall, L. A., Madorsky, S. L., Brown, D. W., Straus, S. and Simha, R., _J. Am. Chem. Soc._ 76, 3430 (1954).

APPENDIX

GLOSSARY OF TRADE NAMES

Trademark or Designation	Composition	Use	Source
Amberol ST-137	heat reactive phenol dialcohol resin	curing agent	Rohm & Haas Co.
CRR0803 resin	heat reactive phenol dialcohol resin	curing agent	Union Carbide Chemical Corp.
Enjay Butyl 268	isoprene-isobutylene copolymer	elastomer	Enjay Chemical Co.
Enjay 3509	ethylene-propylene terpolymer	elastomer	Enjay Chemical Co.
Ethyl Cadmate	cadmium diethyldithio-carbamate	accelerator	R. T. Vanderbilt Co.
GMF	p-quinone dioxime	curing agent	Naugatuck Chemical Div. U. S. Rubber Co.
Hi-Sil 233	precipitated hydrated silica	reinforcing pigment	Columbia Southern Chemical Co.
Hypalon 20	chlorosulfonated polyethylene	elastomer	du Pont
MBTS	benzothiazyl disulfide	accelerator	Monsanto
Neoprene GRT	polychloroprene	elastomer	du Pont
Polar Oil 45	solvent refined petroleum oil	plasticizer	Enjay Co., Inc.
SP1055 resin	bromomethyl, alkylated phenol-formaldehyde resin	curing agent	Schenectady Varnish Co., Inc.

49

APPENDIX (CONT'D)

GLOSSARY OF TRADE NAMES

Trademark or Designation	Composition	Use	Source
TDI Dimer	tolylene 2,4-diisocyanate dimer	curing agent	du Pont
Tellurac	tellurium diethyldithio-carbamate	accelerator	R. T. Vanderbilt Co.

50

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
The Firestone Tire & Rubber Company Central Research Laboratories Akron, Ohio 44317	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

HIGH TEMPERATURE RESISTANT ELASTOMER COMPOUNDS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report - Jan. 64 to Dec. 64

5. AUTHOR(S) (Last name, first name, initial)

Brock, Marlyn J.; Jividen, David L.; Smith, Floyd M.; Rigby, Jack D.; and Thurman, George R.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
July 1965	50	26

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
AF 33(657)-10419	
b. PROJECT NO.	AFML-TR-65-178
7340	
c. Task No.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
734005	--
d.	

10. AVAILABILITY/LIMITATION NOTICES DDC release to CFSTI not authorized. Qualified requestors may obtain copies of this report from the Defense Documentation Center (formerly ASTIA). Dissemination outside the Department of Defense or to recipients other than Government defense contractors is prohibited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Materials Laboratory Air Force Systems Command Wright Patterson AFB, Ohio 45433

13. ABSTRACT

The mechanism by which butyl rubber undergoes thermal degradation in the temperature region 300° to 400°F has been investigated. Gas chromatograph techniques has been used to identify the degradation products and to determine their rates of formation. This investigation indicates that degradation upon heating may be initiated at (a) reactive sites already present in the polymer such as catalyst residues, branching, and terminal unsaturation, (b) oxygenated groups such as hydroperoxides formed during exposure to oxygen and which are unstable at low temperature and (c) other oxygenated groups more stable than hydroperoxides and which do not decompose below 400°F. Compounding evaluations were made of resin cured butyl, reclaimed silicone rubber and ethylene-propylene rubber. A high temperature, high vacuum stress relaxation apparatus was designed and constructed. A limited evaluation program has indicated that the design is satisfactory and the apparatus should prove useful for evaluation of polymers in high vacuum (10^{-5} Torr) and at temperatures up to 500°F. Minor modification would permit testing in an inert gas atmosphere.

DD FORM 1473 (JAN 64)

14.		LINK A		LINK B		LINK C	
KEY WORDS		ROLE	WT	ROLE	WT	ROLE	WT
high temperature resistant elastomers thermal degradation degradation mechanisms compounding investigations physical properties vacuum stress relaxation apparatus							

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (corporate author) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (either by the originator or by the sponsor), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

   (1) "Qualified requesters may obtain copies of this report from DDC."

   (2) "Foreign announcement and dissemination of this report by DDC is not authorized."

   (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

   _____ ."

   (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

   _____ ."

   (5) "All distribution of this report is controlled. Qualified DDC users shall request through

   _____ ."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (paying for) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.